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IMPROVED GRAPHITE FIBER/ACETYLENE TERMINATED MATRIX RESIN PREPREG PRODUCTS

American Cyanamid Company
Chemical Research Division
1937 West Main Street
Stamford, Connecticut 06904

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Acetylene terminated resin formulations were screened and selected in order to provide a composite matrix resin that retained the excellent hot/wet properties of the acetylene terminated resins themselves, but improved on their toughness. Both 2,2' bis(4-3-ethynylphenoxyl phenyl) propane, ATB, and 4,4'-bis(3-ethynylphenoxy)diphenylsulfone, ATS, were combined with various modifiers. Resin formulations were screened in neat resin form and the three formulations having the best balance of toughness and hot/wet properties, as well as good handling characteristics, were scaled-up to tape using unsized AS-4 fiber. A formulation, designated CATB-44, had the best balance of properties and was selected for further optimization. Properties of CATB-44 reinforced with either AS-4, T300, T500, T40, or IM7 were compared. T300 provided the best edge delamination and 90 degree flexural strength, and AS-4 the worst. Of the two intermediate modulus fibers, IM7 was superior. Twenty-five pounds each of T300/CATB-44 and IM7/CATB-44 were produced on commercial production equipment. Samples of the prepreg were provided to five airframe manufacturers (OVER)

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19. Abstract (continued)

and the Air Force Materials Laboratory for evaluation.

SUMMARY

The goal of this program was to develop improved formulations incorporating acetylene terminated resins. In Task I, the base resins were characterized. Also, the cure cycle supplied by the Air Force was compared with a more conventional bismaleimide cure cycle, and was found to give comparative mechanical properties. This indicated that industry-acceptable cure cycles for use in fabricating composite structures were possible. The latter cure cycle was adopted as standard for all formulation work.

Both a preliminary and a comprehensive resin screening procedure were developed. Performance criteria were established and included two sets of target values that were characteristic of: 1) first generation epoxies; and 2) state-of-the-art epoxy and bismaleimides. Fifty-three formulations were evaluated in a preliminary screen and 18 formulations were evaluated in the comprehensive screen. Cure of the formulations, mechanical and thermal properties, toughness and morphology were examined. Formulations incorporating m-ATB acetylene terminated resin were produced that were superior to first generation epoxies and state-of-the-art epoxies and bismaleimides. Three resins were selected for scale up into prepreg. They were selected to give the best balance of toughness and hot/wet properties. After discussion with AFWAL, a redirection was made to expand the evaluation of neat resins to include the mechanical properties of the formulations at 204°C (400°F)/wet and 232°C (450°F)/wet. This redirection was reflected in the selection of the three formulations.

Task II examined the effect of fiber sizing on short beam shear strength at 350, 400, and 450°F. Hot/wet properties of AS-4 laminates were examined, and unsized fiber was found to be better than 'G'-sized fiber. Thus unsized AS-4 was recommended for scale-up.

Five pounds of prepreg, as required for Task II, were prepared on a production tape machine from the three formulations incorporating m-ATB acetylene terminate resin and unsized AS-4 fiber. These materials demonstrated acceptable flow, tack and other handling characteristics. Two of these formulations targeted 218°C (425°F)/wet performance, and the third system targeted 177°C (350°F) hot/wet performance. In addition, further prepreg was fabricated in the laboratory to continue the investigation of resin/fiber interactions. Results from short beam shear tests indicated that the use of unsized T-300 fiber gave results equal to the unsized AS-4 fiber.

At the start of Task III, a bagging and curing procedure was developed that resulted in high quality, void free laminates. The effect of a 150°C intermediate temperature hold, with hold times ranging up to 19 hours was investigated. Based on DSC and mechanical tests of neat resins, a cure cycle with a 1.5 hour hold at 150°C was selected.

The effect of postcuring at 230°C, 250°C, and 300°C was investigated by preparing $(0/\pm 45/0)_s$ laminates. No microcracking was found after any of the postcure temperatures, but glass transition measurements indicated that the 300°C postcure temperature degraded the resin. Additional postcure studies on $(0/\pm 90/0)_s$ laminates indicated no microcracking on specimens postcured at 230°C. Cracking observed on laminates postcured at 250°C appeared to be caused by fiber/resin debonding. Since only a slight difference in glass transition temperature between specimens postcured at 230°C and 250°C was observed, the 230°C postcure temperature was selected to prepare laminates for comprehensive physical evaluations.

The laminate properties of m-ATB formulations CATB-44/AS-4, CATB-44/AS-4 and CATB-51/AS-4 were measured. Ultrasonic examination of the laminates showed no voids or compaction problems. In dry tests at 73°F, 350°F and 450°F, the 0° flexural properties of

the CATB laminates were comparable to CYCOM® 985 (epoxy) and CYCOM® 3100 (BMI) and approached or exceeded the target values of this program. Under these conditions, the interlaminar shear properties of the CATB laminates fell somewhat short of the target values, but were similar to the commercial prepregs. A shear failure mode was observed in all CATB formulations under all conditions. In hot/wet tests at 350°F, the CATB formulations have higher flexural and interlaminar shear strengths than the CYCOM 3100 baseline BMI control. At 425°F/wet the CATB systems are still capable of bearing load. The edge delamination strengths of the $(+30,-30_2,+30,90)_s$ CATB/AS-4 laminates are found to be midway between the state-of-the-art CYCOM 3100/AS-4 BMI and the state-of-the-art CYCOM 985/AS-4 epoxy systems. These results showed the superior hot/wet performance of the CATB materials over both baseline materials, with no sacrifice in toughness when compared to CYCOM 3100 bismaleimide.

Additional mechanical property determinations on CATB-44 were conducted on a laminate which was postcured at 250°C, instead of the standard 230°C used in the program to date. Significant hot/wet property improvement was noted with this higher postcure temperature.

Fracture surface analysis of m-ATB formulation laminates indicated that there was a larger amount of resin debonding from AS-4 fiber than is normally seen with epoxy matrix resins. This suggested that an improvement in composite properties might be possible with an improvement in the resin/fiber interface, either through a change in the fiber or the fiber sizing.

All m-ATB formulations survived thermal aging without evidence of microcracking.

The effort to develop an improved formulation incorporating m-ATS resin began with its chemical and physical characterization. The standard cure cycle developed for m-ATB formulations was also

found to be useful for m-ATS resin and m-ATS formulated systems. Twenty-four m-ATS formulations were examined in the preliminary screen and ten underwent comprehensive evaluation. The toughness and elevated temperature performance of the m-ATS formulations was within the range seen for the m-ATB formulations. No significant improvements were obtained by postcuring at 300°C versus the standard 250°C condition. Because of the other favorable attributes of the m-ATB formulations compared to the m-ATS formulations, such as tack, a contract modification was proposed and approved. This modification focused the remaining work on additional improvements in the m-ATB laminates.

The modification permitted a more extensive development of m-ATB formulation laminates by evaluating the effect of five different fibers on the composite's fiber/resin adhesion and in-plane hot/wet performance. Based on the results of this study, two CATB-44/fiber combinations were recommended and approved for scale-up into prepreg for AFWAL evaluation. The fibers were Amoco's THORNEL® T-300 and Hercules' MAGNAMITE® IM7.

Two thirty-pound lots of prepreg were produced and sampled to five air frame manufacturers for testing. Five pounds were used to test the effect of film interleafing on composite toughness.

Finally, heat aging in air at 400°C for up to 200 hours did not reduce CATB-44 toughness and actually increased the glass transition temperature by 30°C.

FOREWORD

This Final Technical Report covers work performed in Contract No. F33615-84-C-5050, entitled, "Improved Graphite Fiber/Acetylene Terminated Matrix Resin Prepreg Products" was performed during the period 1 February 1985 to 24 August 1987. This program was sponsored by the Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Forve Base, Ohio. The Project Scientist was Dr. Frederick Hedberg.

Mr. Robert E. Evans was the Cyanamid Project Manager, and Dr. Dalip K. Kohli and Dr. Jeanne L. Courter were the successive Principal Investigators. Mr. Stnaley S. Kaminski was responsible for carrying out the fiber-resin adhesion evaluation and Mrs. Ann Cronin carried out testing throughout the program.

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1.0 INTRODUCTION

1.1 BACKGROUND

The Air Force Aeronautical Laboratories developed a number of high temperature polymers based on the cure of acetylene terminated oligomers [1-72]. The acetylene moiety crosslinked around 177°C (350°F) via an addition reaction to give void free laminates. One could use "epoxy-like" cure cycles in conventional equipment, followed by a free standing postcure at 250°C to develop high temperature properties. The resulting polymer had high thermo-oxidative stability and a high glass transition temperature. Elevated temperature properties, especially in the presence of moisture, were much better than could be achieved by epoxy resins [64].

Two of the most promising monomers that emerged from the Air Force's work were 2,2[1] bis(4-[3-ethynylphenoxy]phenyl)propane (m-ATB) [68] and 4,4[1]-bis(3-ethynylphenoxy)diphenyl sulfone (m-ATS) [65-72]. These resins had the potential for low cost manufacture as well as excellent pot life and processability.

However, a major drawback with all of the acetylene terminated (AT) polymers was their low toughness. The low strain-to-failure of the AT resins, combined with their high shrinkage, resulted in laminates with a large number of microcracks and poor mechanical performance.

1.2 PROGRAM OBJECTIVE

The objective of this program was to develop an improved graphite fiber/acetylene terminated matrix resin prepreg product. Formulations containing ATB resin were designed to provide improved toughness and other mechanical properties while maintaining 350°F to 450°F service temperature capability. Not only was 177°C (350°F)/wet and 232°C (450°F)/dry performance

required, but 204°C (400°F)/wet and 232°C (450°F)/wet performance were also required. Performance optimization through fiber choice and interleaf investigation was assessed. Samples of graphite tape prepreg with the optimized formulations were prepared.

1.3 PROGRAM APPROACH

Within the original scope of the contract, the program had been divided into the following tasks to be completed within the original program schedule.

TASK I

- For both the ATB and ATS resins, formulate and conduct preliminary resin screening of a minimum of 50 matrix systems. Compare mechanical and thermal performance against target values.

- Characterize and conduct comprehensive evaluations of at least 12-15 neat resins using formulations prepared from both the ATB and ATS acetylene terminated resin systems. Mechanical, thermal and rheological performance will be compared to a set of target values.

TASK II

- Conduct preliminary laminate tests to assess fiber/resin compatibility with AS-4 as well as other fibers, if necessary. Using a production tape machine, prepare 100 ft^2 of prepreg material for each of the three most promising formulations of both the ATB and ATS formulations identified during the neat resin screening evaluations.

TASK III

- Fabricate laminate panels from these prepregs and measure toughness and upper use temperature related mechanical properties. These mechanical properties will be compared both with a set of target values and with the measured values of a state-of-the-art epoxy, CYCOM 985, and a state-of-the-art bismaleimide, CYCOM 3100.

TASK IV

- Prepare up to 100 lbs. of additional prepreg material utilizing the formulation found to be the most promising with respect to processing characteristics and composite mechanical properties for delivery to AFWAL/MLBC.

With the approval of the contract redirection, Task IV was modified as follows:

TASK IV

- Characterize and evaluate ATB matrix resin/graphite fiber combinations, identifying the optimum ATB formulation and form. This will be accomplished by studying three parameters:

  1. Long term heat aging effects on ATB neat resin
  2. Influence of fiber on laminate mechanical properties
  3. Toughness enhancement by high strain film interleaving

- Prepare up to 100 lbs. of prepreg material utilizing the fiber/resin combination(s) found to be most promising with respect to processing characteristics and composite mechanical properties for delivery to AFWAL/MLBC.

2.0 TASK I: NEAT RESIN FORMULATION

2.1 BASE RESIN CHARACTERIZATION

2.1.1 m-ATB

For use in Tasks I-III, an 8 lb. sample of m-ATB resin (Fluorochem) was received from the Air Force Materials Laboratory. m-ATB's structure is shown in Figure 2.1. The resin was a dark brown viscous liquid at room temperature. In order to compare future material with the initial material, chemical and mechanical characterization of this resin was conducted.

Chemical Characterization

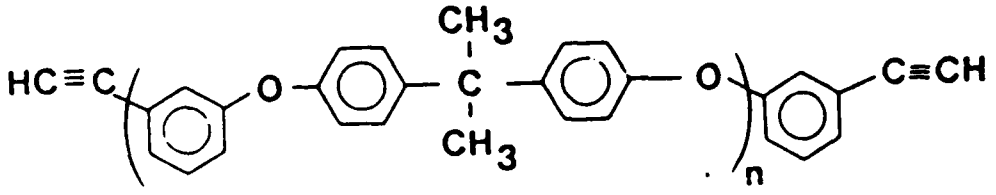
The m-ATB resin was analyzed by NMR (H^1 and C^{13}), IR, HPLC and GPC. For both HPLC and GPC, detector wavelength was set at 220 nm. The m-ATB resin has been observed to be partly insoluble in acetonitrile. Therefore, the HPLC curve represents only the acetonitrile soluble material.

Both the HPLC and proton NMR indicate a monomer content of about 60%, the remainder being oligomers or other products. GPC analysis showed the presence of about eight components, the concentration of the major component being about 68%. The IR spectrum did not show the -C=C- absorption, probably due to the symmetry of the m-ATB molecule.

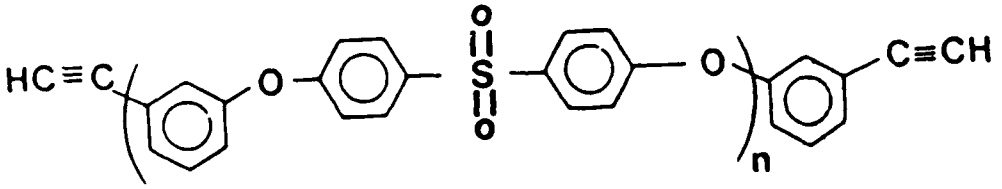
The HPLC, IR, GPC, and 200 MHz proton NMR spectra of m-ATB are shown in Figures 2.2 to 2.5.

Thermal Analysis

Differental Scanning Calorimetry (DSC) indicated that the exothermic cure consisted of a single symmetrical peak with a maximum at 241°C (466°F) and a total heat of reaction of 561 J/g

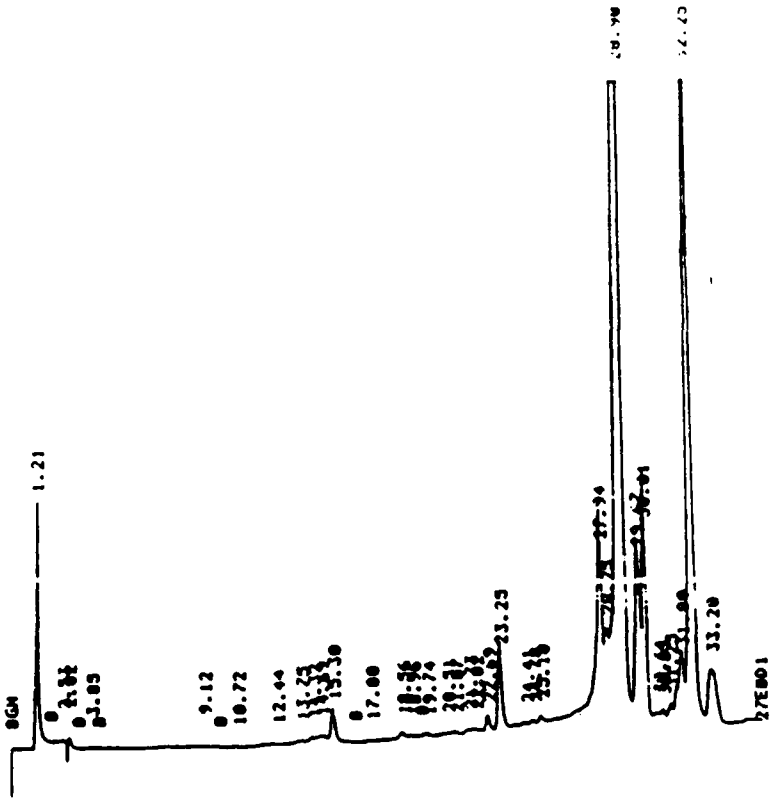


ATB



ATS

FIGURE 2.1 CHEMICAL STRUCTURE OF m-ATB AND m-ATS



TIME	AREA	BC	RRT	RF	C	NAME
1.21	11.9936		0.121	1.000	1.9582	
2.53	2.6712	V	0.253	1.000	0.4361	
2.85	1.8288		0.282	1.000	0.2981	
3.85	0.0479		0.385	1.000	0.0078	
9.12	0.2231		0.912	1.000	0.0364	
10.72	0.0895	V	1.072	1.000	0.0146	
12.44	0.5651	T	1.244	1.000	0.0923	
13.75	0.7057	T	1.375	1.000	0.1152	
14.32	1.1293	T	1.432	1.000	0.1844	
14.69	1.5445	T	1.469	1.000	0.2522	
15.30	3.2059		1.530	1.000	0.5234	
17.00	0.0451	V	1.700	1.000	0.0074	
18.56	0.6090	T	1.856	1.000	0.0994	
18.96	0.1347		1.896	1.000	0.0220	
19.74	0.2796	V	1.974	1.000	0.0457	
20.51	0.3393	T	2.051	1.000	0.0554	
21.87	0.0066	T	2.187	1.000	0.0027	
21.73	0.5181	T	2.173	1.000	0.0846	
22.02	1.0154	T	2.202	1.000	0.1658	
22.69	1.6076	T	2.269	1.000	0.2625	
23.25	7.8016	T	2.325	1.000	1.2968	
24.41	2.5238	T	2.441	1.000	0.4119	
24.78	1.4044	T	2.478	1.000	0.2293	
25.18	1.8747	T	2.518	1.000	0.3061	
27.94	35.3190	T	2.794	1.000	5.7665	
28.25	9.1254	T	2.825	1.000	1.4899	
28.98	370.5836	T	2.898	1.000	60.4928	
29.67	18.5644	T	2.967	1.000	3.0310	
30.01	18.7364	T	3.001	1.000	3.0624	
30.61	1.7987	T	3.061	1.000	0.2937	
30.85	1.5466	T	3.085	1.000	0.2525	
31.25	2.2456	T	3.125	1.000	0.3666	
31.88	9.8950	T	3.188	1.000	1.6156	
32.25	92.3443	T	3.225	1.000	15.0779	
33.20	9.6438	V	3.320	1.000	1.5745	

FIGURE 2.2 HPLC TRACE FOR m-ATS RESIN

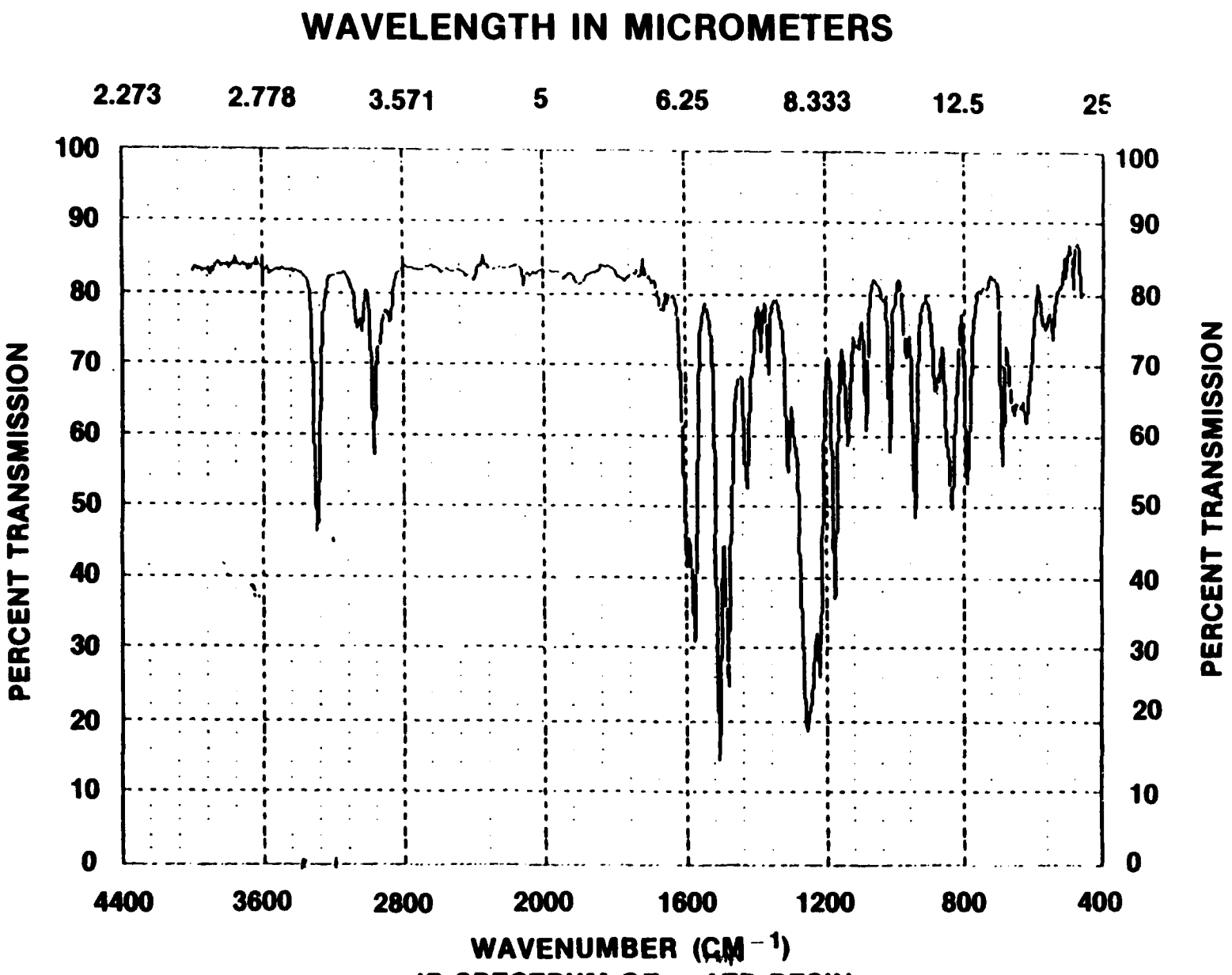
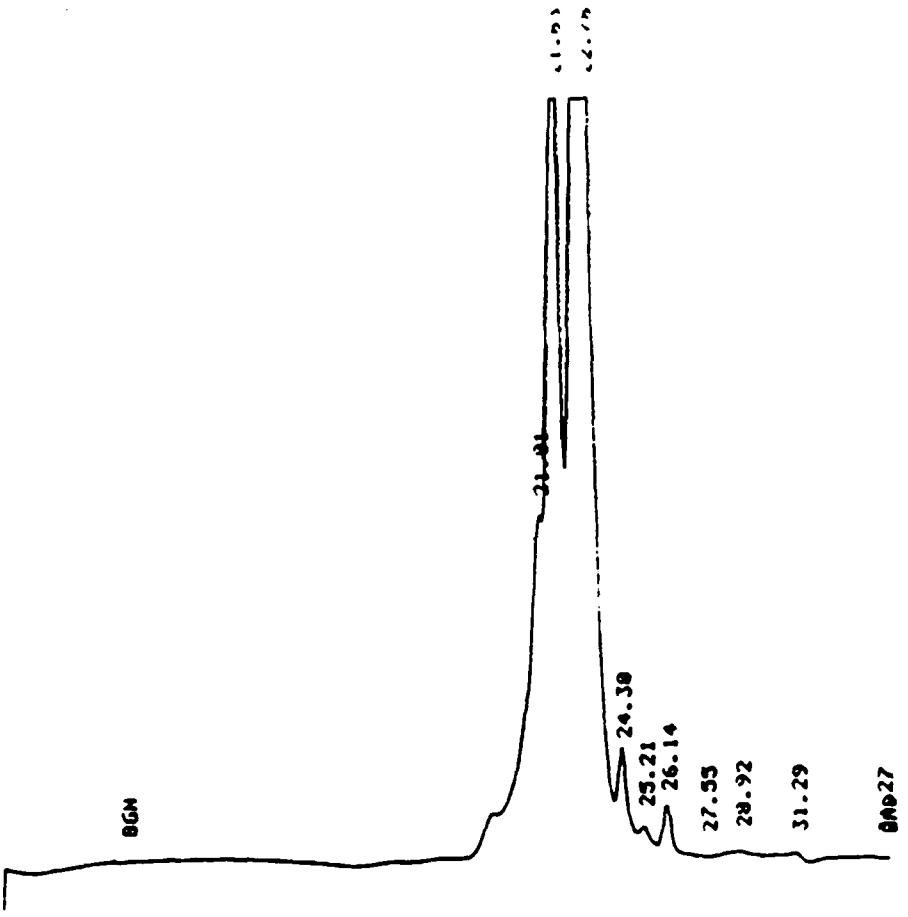
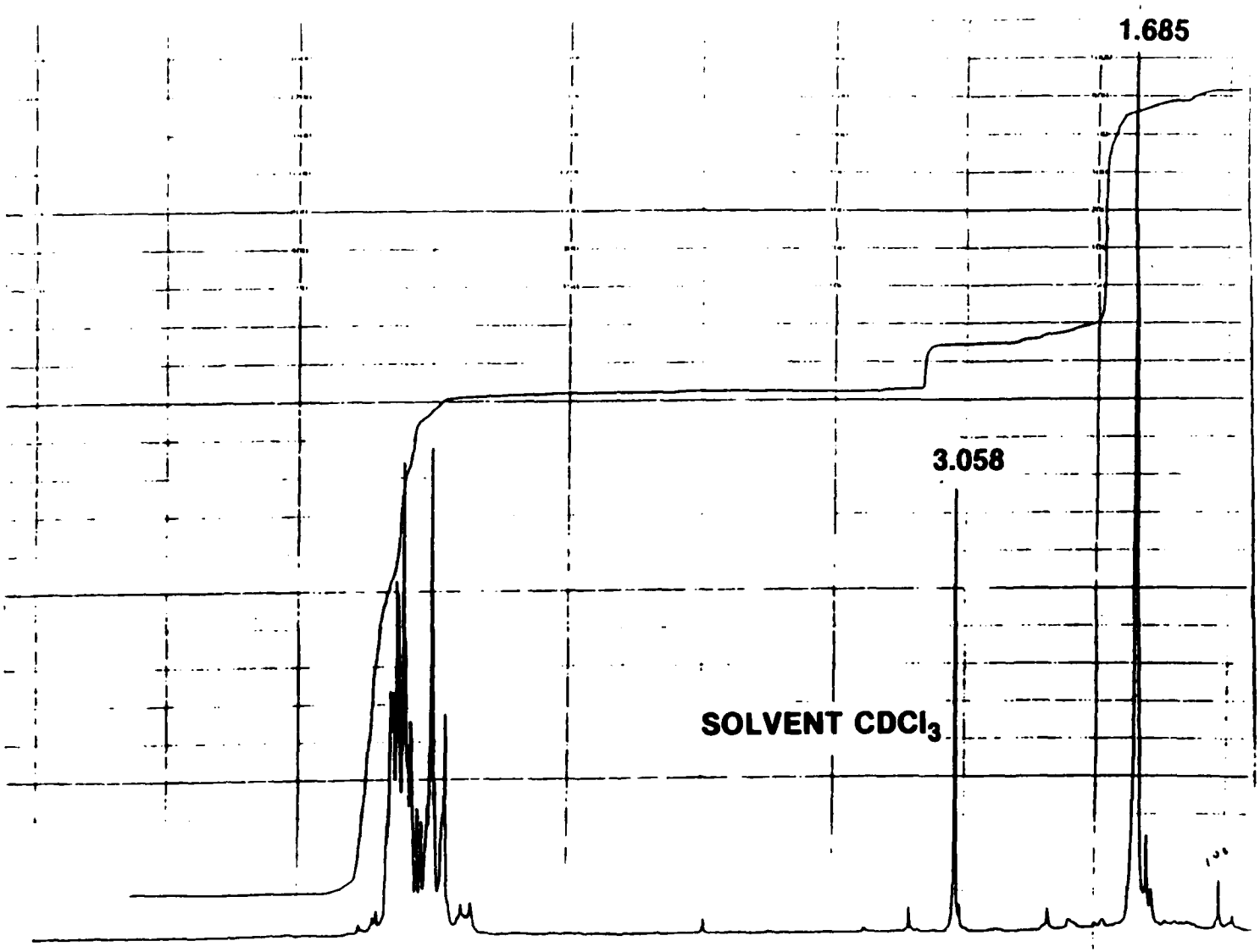


FIGURE 2.3 IR SPECTRUM OF m-ATB RESIN



TIME	AREA	BC	RRT	RF	C	NAME
21.01	85.9935	T	2.101	1.000	8.1404	
21.63	202.7000	T	2.163	1.000	19.1878	
22.76	721.5104	T	2.276	1.000	68.2987	
24.30	18.0390	T	2.430	1.000	1.7076	
25.21	7.0240	T	2.521	1.000	0.6649	
26.14	10.1254	T	2.614	1.000	0.9585	
27.55	1.0040	T	2.755	1.000	0.0950	
28.92	5.0102	T	2.892	1.000	0.5588	
31.29	4.0099	U	3.129	1.000	0.3796	
34.27	0.1859		3.427	1.000	0.0176	

FIGURE 2.4 GPC TRACE FOR m-ATB RESIN



FIGURF 2.5 **PROTON NMR SPECTRUM FOR m—ATB RESIN**

(134 cal/g) when scanned at 10°C/min.

Mechanical Properties

A 1.6 mm (1/16 inch) thick neat resin plaque was cast between glass plates using Vydax mold release. The casting was cured by the cure cycle developed by the Air Force Materials Laboratory which consisted of 15 h at 140°C (285°F) and 5 h at 170°C (338°F) in air, followed by a postcure of 4 h at 250°C. The complete cure cycle with heating rates is shown below:

Hold at 80°C for 1 h
80°C to 140°C at 1°C/min
Hold at 140°C for 15 h
140°C to 170°C at 1°C/min
Hold at 170°C for 5 h
170°C to 250°C at 1°C/min
Hold at 250°C for 4 h
Cool to RT at 2°C/min

The glass transition temperatures and the flexural stress-strain properties of m-ATB resin, measured using procedures described in Appendix A, are shown in Table 2.1. For comparison, the resin properties of a first generation epoxy, a state-of-the-art epoxy, CYCOM 985, and a state-of-the-art BMI, CYCOM 3100 are included. The ATB's stress-strain properties were equal to first generation epoxies but less than state-of-the-art epoxy BMI. The dry glass transition temperture of m-ATB was 282°C compared to 333°C for CYCOM 3100.

The 177°C (350°F) hot/wet modulus of m-ATB is higher than that of a BMI, but both systems met our initial target value of 2.24 GPa (0.325 MSI). Hot/wet conditioning consisted of immersion in water at 71°C (160°F) for 2 weeks. ATB resin did not pick up water after the first 24 hours reaching a moisture content of 0.24% $\pm$ 0.02%.

TABLE 2.1

HEAT RESIN FLEXURAL PROPERTIES

Resin	Tg, °C Dry/Wet	Water Absorption, %	Dry Modulus GPa	(MSI)	Wet Modulus* GPa	(MSI)	Strength MPa	(KSI)	Strain %	Work-to-break MJ/m^3	($in\text{-}lb/in^3$)	G_{IC} J/m^2	$in\text{-}lb/m^2$
m-ATB	282/263	.20	3.78 ± .04	(.548 ± .006)	2.72 ± .03	(.396 ± .005)	111 ± 12	(16.1 ± 1.8)	3.1 ± 0.4	1.66 ± .41	(240 ± 60)	75	.43
MY720/DDS/ BF_3 MEA	285/222	4.9	4.14	(.601)	--	--	105	(15.2)	2.5	1.41	(205)		
Cycom® 985 Epoxy	228/175	5.1	4.06	(.590)	--	--	155	(22.5)	4.5	3.93	(570)		
Cycom® 3100	333/-	3.9	4.71	(.683)	2.27	(.329)	177	(25.7)	4.1	4.69	(680)	96	0.55
m-ATS	338/-	-	3.93	(.570)	--	--		(10.9)	1.9	0.76	(110)		

*Tested at 177°C (350°F) after two weeks in water at 71°C (160°F)

Cure Cycle Development

In an attempt to develop a simpler cure cycle which would permit an industrially acceptable composite manufacturing schedule, m-ATB resin was cured using a cycle used for bismaleimide resins. The cure schedule was as follows:

Hold at 150°C for 1.5 h
150°C to 177°C at 1.5°C/min
Hold at 177°C for 4 h
177°C to 250°C at 5°C/min
Hold at 250°C for 4 h
Cool to RT at 2°C/min

A high quality casting was obtained. The comparison of dynamic mechanical properties of m-ATB resin cured using the Air Force and the Cyanamid cycles is shown in Table 2.2, and the stress-strain performance and water pickup are shown in Table 2.3.

A slightly lower strain to failure and dry modulus were found with the shorter cure. However, based on other statistical studies of batch-to-batch properties, these differences are not statistically significant. Therefore, this short cure cycle was used for the remainder of the program.

2.1.2 m-ATS

Work was started on the formulation of m-ATS resin with the arrival of 7.5 lbs. of monomer from Fluorochem, Inc. Initial work focused on chemical characterization of m-ATS resin and determination of its thermal and mechanical properties.

Chemical Characterization

Chemical characterization of m-ATS was carried out by NMR (H^1 and C^{13}), IR, HPLC, and GPC. The HPLC analysis showed about

TABLE 2.2

Comparison of Cure Cycles - Glass Transition Temperatures, for m-ATB

Property By Dynamic Mechanical Analysis	Tg (°C) AF Cure Cycle		Tg (°C) Cyanamid Cure Cycle	
	Dry	Wet	Dry	Wet
Tan Delta Peak	282	266	276	264
Modulus Intersept	248	234	249	232
5% Offset	197	186	200	185

TABLE 2.3
Comparison of Cure Cycles - Flexural Stress-Strain Performance
For m-ATB

Composition	Conditioning	Modulus GPa (MSI)	Strength MPA (KSI)	Strain (%)	Work-to-Break MJ/m^3 ($in\text{-}lb/in^2$)	Water Absorption, %
m-ATB with AF Cure Cycle	RT/ Dry	3.78 ± .04 (0.548 ±0.006)	111 ± 12.4 (16.1 ±1.8)	3.1 ±0.4	1.66 ±.41 (240 ±60)	--
	350°F/ Wet	2.73 ± .03 (0.396 ±0.005)	86.8 ± 6.2 (12.6 ±0.9)	3.5 ±0.3	1.66 ±.27 (240 ±40)	0.20%
m-ATB with Cyanamid Cure Cycle	RT/ Dry	3.69 ± .011 (0.535 ±0.001)	90.2 ± 3.4 (13.1 ±0.5)	2.5 ±0.1	1.38 ±.10 (200 ±15)	--
	350°F/ Wet	2.79 ± .04 (0.405 ±.006)	79.2 ± 5.5 (11.5 ±.8)	3.0 ±.2	1.39 (201 ±30)	0.23%

fifteen components, the major component being about 67%. The NMR and IR analysis confirmed the m-ATS structure. The NMR (H^1 and C^{13}), IR, HPLC, and GPC spectra of m-ATS are shown in Figures 2.6 to 2.10, respectively. The m-ATS resin was a dark brown glassy solid at room temperature.

Thermal Analysis

The DSC thermogram for the cure of m-ATS consisted of a single symmetrical exothermic peak with a maximum at 227°C, and having a heat of reaction of 461 j/g (110 cal/g) at a heating rate of 10°C/min.

Mechanical Properties

A 1.6 mm (1/16 inch) thick neat resin plaque was cast between glass plates using Freekote 44 mold release following the standard resin casting procedure which was used for m-ATB resin evaluations. The casting was cured by the following cure cycle:

Hold at 150°C for 1.5 h
150°C to 177°C at 1.5°C/min
Hold at 177°C for 4 h
177°C to 250°C at 5°C/min
Hold at 250°C for 4 h
Cool to RT at 2°C/min

A high quality casting was obtained. The dynamic mechanical properties and the dry flexural properties are shown in Table 2.3. For comparison, m-ATB neat resin properties obtained from the same cure cycle are also shown in Table 2.3. As expected, m-ATS had a higher glass transition temperature and a higher modulus than m-ATB, but a somewhat lower strength and strain to failure. It also has higher wet moduli between 350°F to 450°F. In fact, it has a higher wet modulus at 450°F than m-ATB has at 400°F/wet.

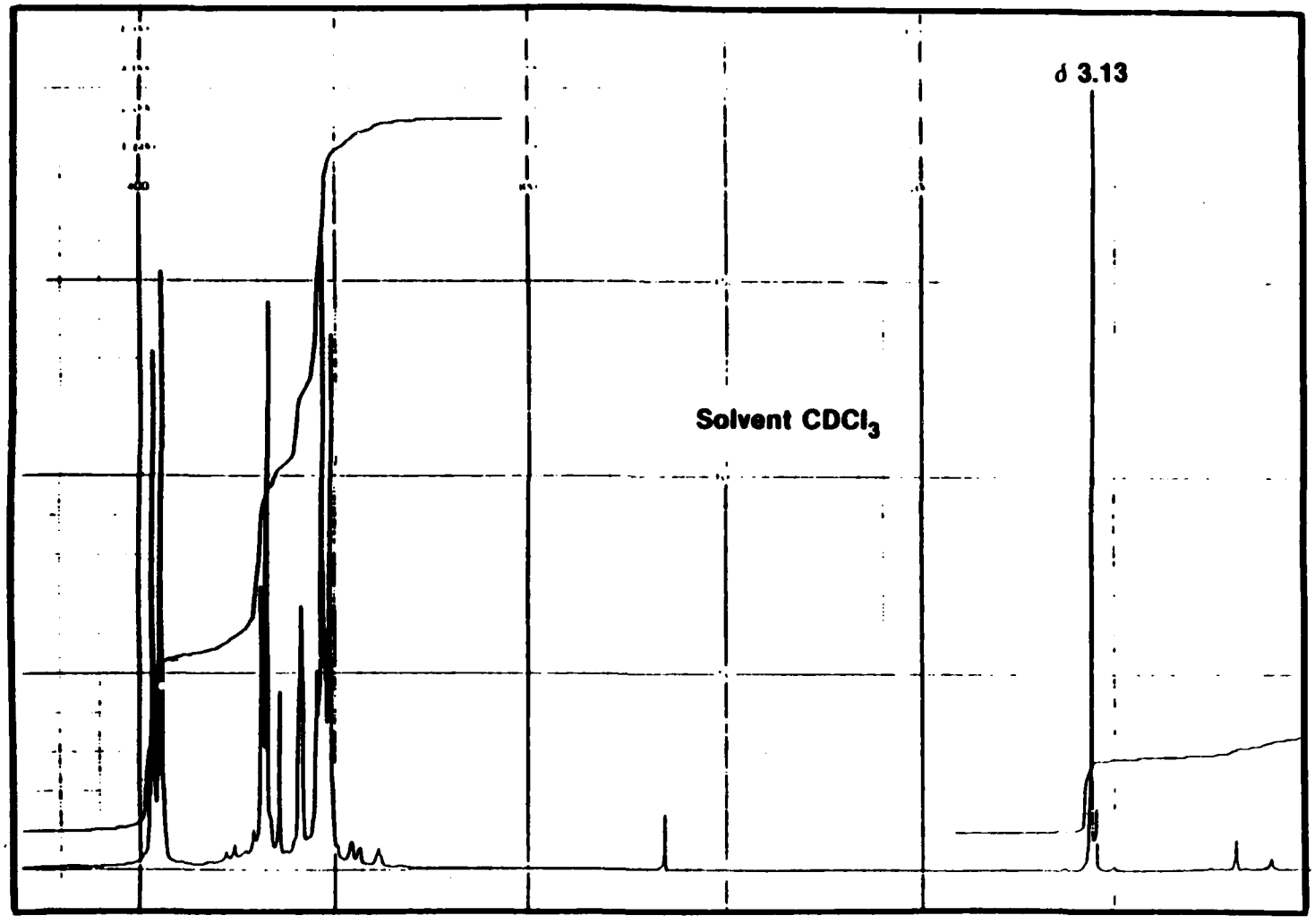


FIGURE 2.6 **PROTON NMR SPECTRUM OF m-ATS RESIN**

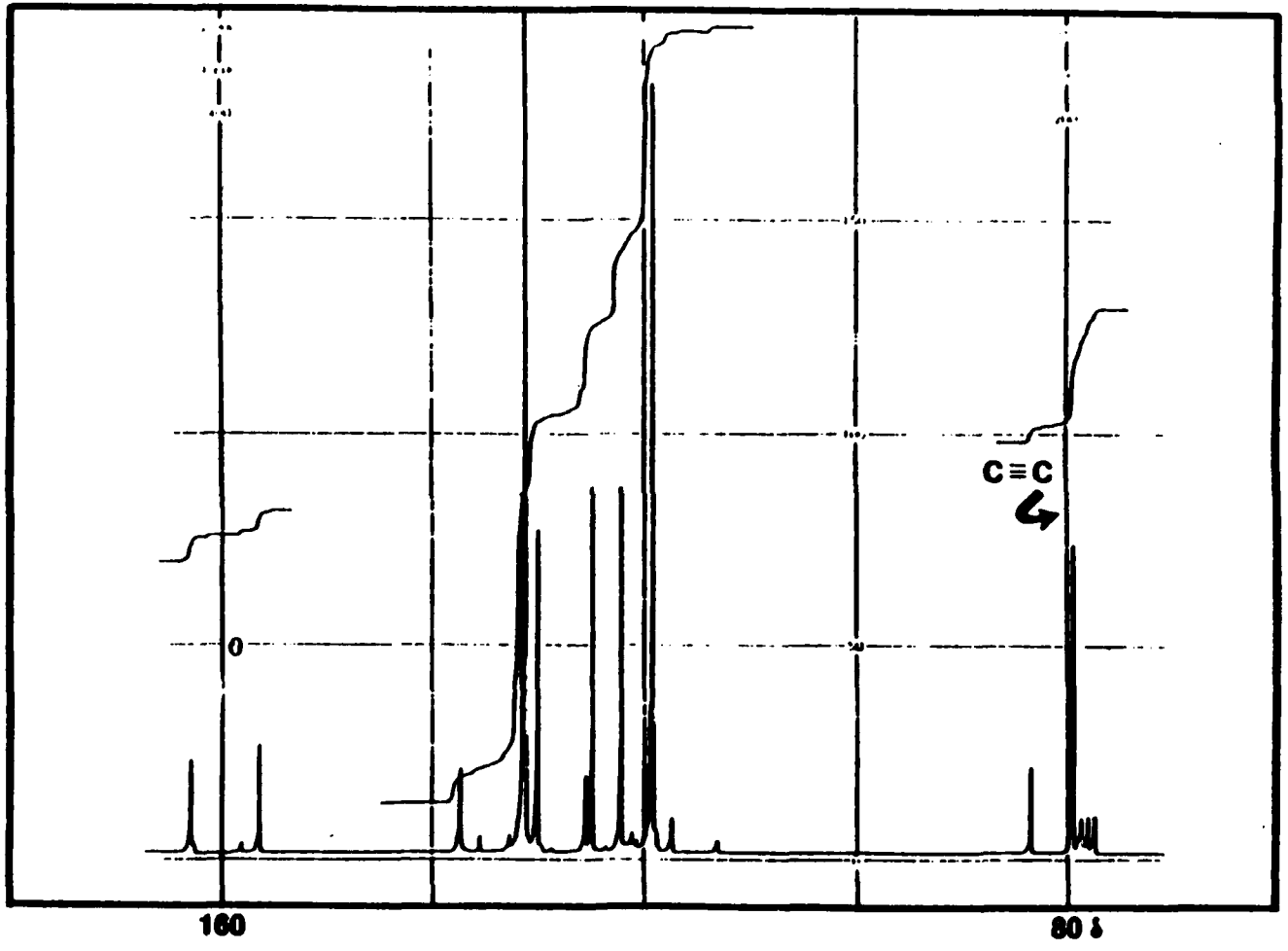


FIGURE 2.7 **CARBON-13 NMR SPECTRUM OF m-ATS**

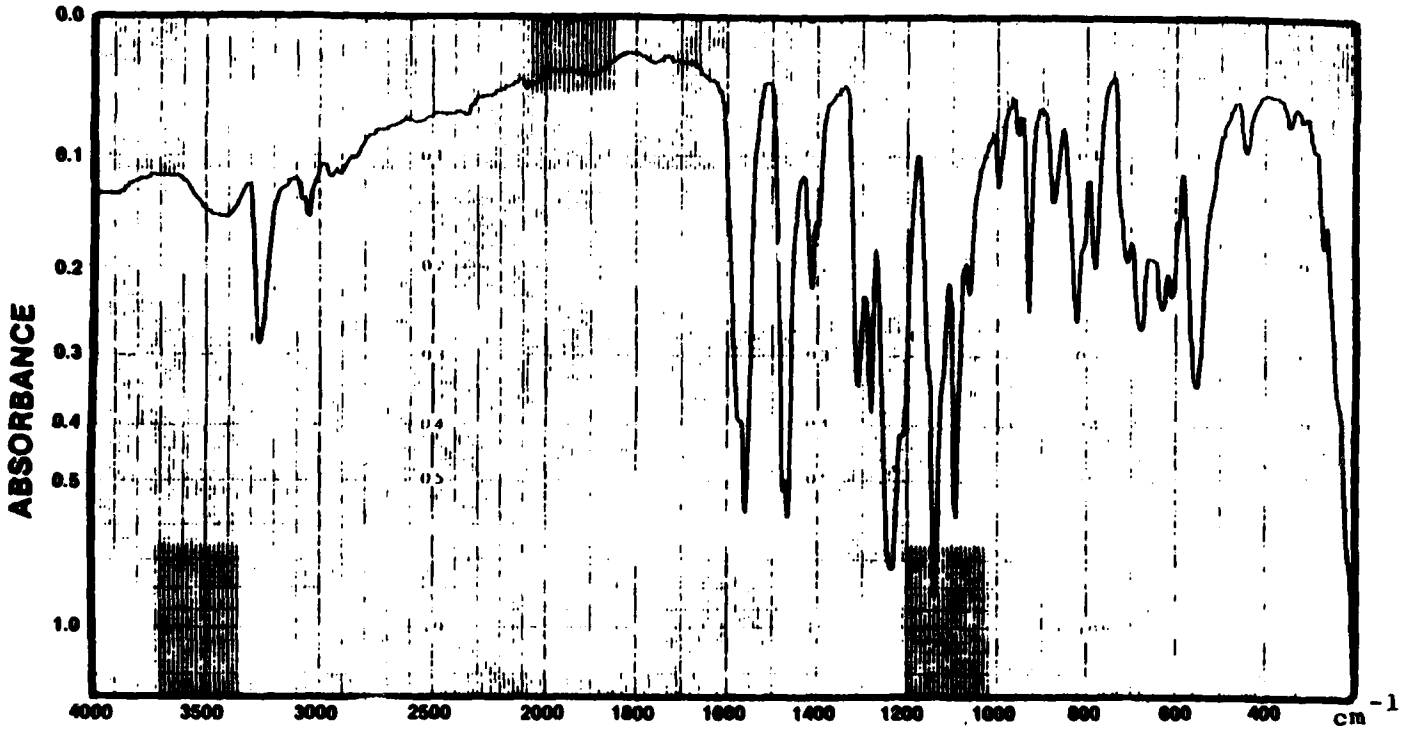


FIGURE 2.8 **IR SPECTRUM OF m-ATS RESIN**

TIME	AREA	BC	RRT	RF	C
1.03	0.0330	V	0.103	1.000	0.0065
1.29	0.0626	T	0.129	1.000	0.0123
1.51	0.1537		0.151	1.000	0.0302
2.99	2.2203	T	0.299	1.000	0.4371
3.49	1.7156	T	0.349	1.000	0.3365
3.99	4.3553	T	0.399	1.000	0.8543
4.81	1.2117		0.481	1.000	0.2377
9.73	0.2866		0.973	1.000	0.0562
10.85	0.5861	T	1.085	1.000	0.1150
11.31	0.0827	T	1.131	1.000	0.0162
11.81	0.2924	V	1.181	1.000	0.0574
13.12	0.4377	T	1.312	1.000	0.0859
15.86	1.9264	T	1.586	1.000	0.3779
18.08	0.4043		1.808	1.000	0.0793
18.58	0.2435	T	1.858	1.000	0.0478
19.04	0.2327	T	1.904	1.000	0.0456
19.39	0.0900	V	1.939	1.000	0.0176
20.18	7.5235	T	2.018	1.000	1.4758
20.70	0.6902	T	2.070	1.000	0.1354
21.26	0.8549	V	2.126	1.000	0.1677
22.06	4.0401	T	2.206	1.000	0.7941
22.67	0.3319	T	2.267	1.000	0.0651
22.96	1.5699	T	2.296	1.000	0.3079
23.52	20.2790	V	2.352	1.000	3.9778
24.61	11.0822	T	2.461	1.000	2.1581
25.16	1.6409	T	2.516	1.000	0.3219
25.72	343.4496	T	2.572	1.000	67.3683
26.40	1.6228	T	2.640	1.000	0.3183
27.02	11.7676	T	2.702	1.000	2.3083
27.48	8.9676	T	2.748	1.000	1.7590
28.01	3.0099	T	2.801	1.000	0.5904
28.31	63.5033	T	2.831	1.000	12.4563
28.83	1.7706	T	2.883	1.000	0.3473
29.11	1.7961	T	2.911	1.000	0.3523
29.32	2.4043	T	2.932	1.000	0.4716
29.65	7.2512	V	2.965	1.000	1.4223
30.16	0.9243		3.016	1.000	0.1813
30.43	1.0570	V	3.043	1.000	0.2073

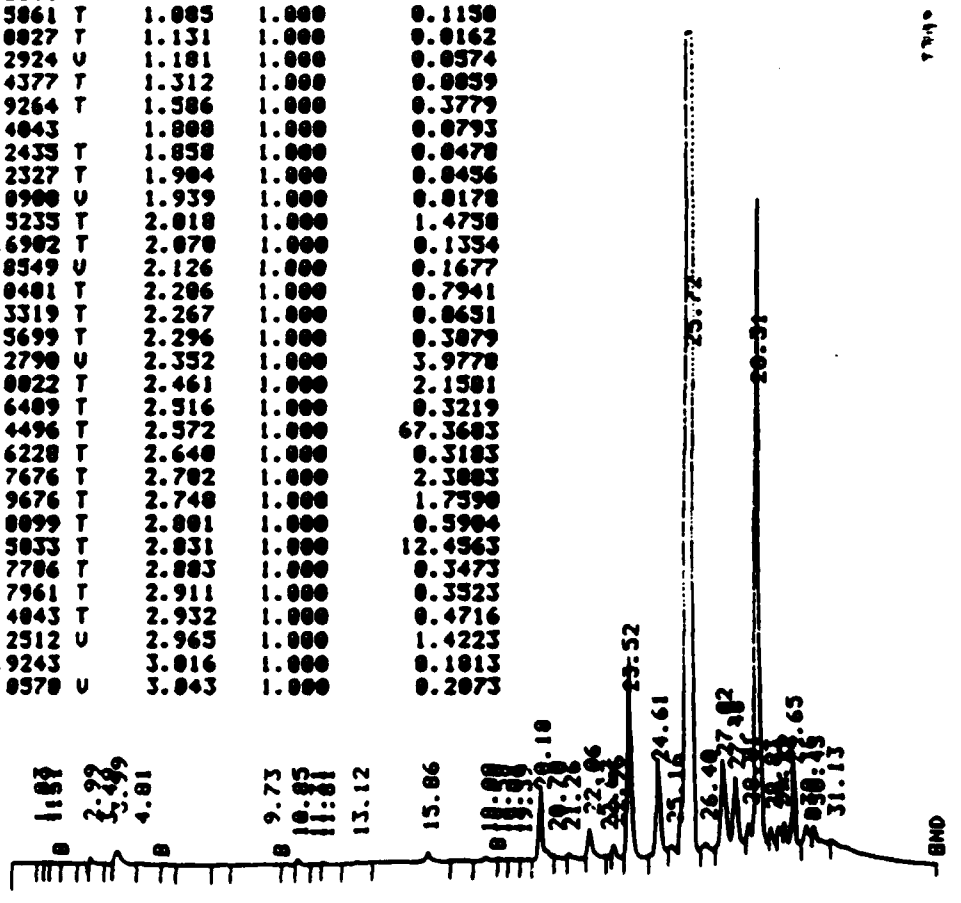
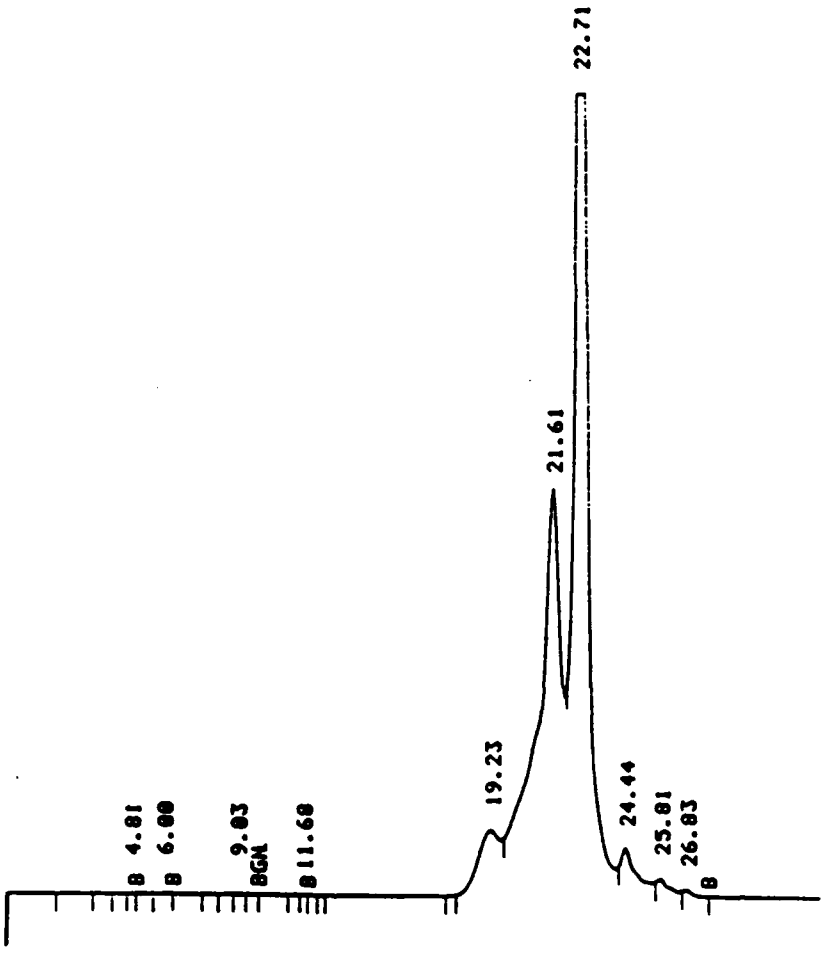


FIGURE 2.9 HPLC TRACE FOR m-ATS RESIN



TIME	AREA	BC	RRT	RF	C
11.68	0.0250		1.168	1.000	0.0067
19.23	18.6835	T	1.923	1.000	4.9753
21.61	128.8440	T	2.161	1.000	34.3103
22.71	212.0294	T	2.271	1.000	56.4617
24.44	11.5424	T	2.444	1.000	3.0736
25.81	3.4478	T	2.581	1.000	0.9181
26.83	0.9548		2.683	1.000	0.2543

FIGURE 2.10 GPC TRACE FOR m-ATS RESIN

Cure Cycle Development

The Air Force Materials Laboratory developed a cure cycle for m-ATS which required a long hold at 140°C and a postcure temperature of 300°C. In order to compare m-ATS neat resin properties obtained with the Cyanamid cure cycle with those obtained with the AF cure cycle, m-ATS resin casting was cured by the following AF cure cycle:

Hold at 140°C for 24 h
Ramp to 177°C
Hold at 177°C for 5 h
Postcure at 300°C for 10 h
Cool at 2°C/min to RT

To determine the effect of postcure temperature, m-ATS was cured by the Cyanamid cure cycle but with a 300°C/4h postcure instead of 250°C/4h.

All three cure cycles provided void free high quality castings. The comparison of physical property data from these three cure cycles is shown in Table 2.4. All cure cycles gave similar stress-strain properties at room temperature. However, at elevated temperature, the wet properties were found to be significantly better for m-ATS resin cured by Cyanamid cure cycle (1.5 h 150°C, 4 h 177°C, 4 h postcure at 250°C) than the other two cure cycles. Also the glass transition temperature obtained with this cure cycle was found to be the same as that obtained with a postcure temperature of 300°C.

Thus, the following cycle was used for the remainder of the program:

1.5 h 150°C
4 h 177°C
Postcure 4 h 250°C

TABLE 2.4

m-ATS NEAT RESIN PROPERTIES CURED BY DIFFERENT CURE CYCLES

CATS # Formulation	Condition	Modulus E (MSI)	Strength (KSI)	Strain to Failure %	Work to Break in-lb/in³	Glass Transition, Tg°C Tan	MI	5% Offset
1) m-ATS with Cyanamid Cure	RT	0.574	9.2	1.6	75	342	280	276
		±0.012	±0.9	±0.1	±15			
cure cycle 1.5 h 150°C	350°F/wet	0.459	6.9	1.5	55			
		±0.007	±1.0	±0.2	±15			
4 h 177°C	400°F/wet	0.379	7.7	2.1	-			
		±0.038	±2.2	±0.6				
4 h 250°C	450°F/wet	0.331	6.6	2.1	-			
		±0.008	±0.9	±0.3				
2) m-ATS with AF Cure	RT	0.548	10.0	1.7	80	327	278	270
		±0.013	±1.6	±0.1	±10			
cure cycle 24 h 140°C	350°F/wet	0.433	8.8	1.9	70			
		±0.048	±2.4	±0.3	±15			
5 h 177°C	400°F/wet	0.299	5.6	2.0	-			
		±0.052	±1.4	±0.4				
10 h 300°C	450°F/wet	0.295	8.8	3.4	-			
		±0.003	±0.2	±0.1				
3) m-ATS with Cyanamid Cure/ 300°F postcure	RT	0.553	11.6	2.1	130	339	281	266
		±0.015	±3.0	±0.5	±65			
cure cycle 1.5 h 150°C	350°F/wet	0.427	9.6	2.2	110			
		±0.010	±1.1	±0.2	±25			
4 h 177°C	400°F/wet							
4 h 300°C	450°F/wet	0.308	7.3	2.6	-			
		±0.010	±1.8	±0.7				

Effect of Moisture on m-ATS Cured by Different Cure Cycles

The rate of water absorption over a period of up to two weeks for m-ATS resin cured by various cure cycles is shown in Table 2.5. These results indicate that the m-ATS cured by AF cure cycle absorbs water at a faster rate than m-ATS cured by other cure cycles.

2.2 m-ATB FORMULATIONS

Several formulation strategies were chosen to overcome the limitations of m-ATB, based on previous work with bismaleimide resin toughening. They included a) lowering the crosslink density; b) second phase toughening; c) interpenetrating networks, and d) reactive/non-reactive modifiers.

General goals in formulating were to a) maintain the necessary Tg; b) provide the necessary 177-232°C (350-450°F) hot/wet modulus; c) increase room temperature strain at break and toughness; d) reduce resin shrinkage; e) to maintain tack and out time; f) have no odor, and g) use non-toxic formulation materials.

The initial target was to exceed the room temperature mechanical performance and toughness of first generation epoxy matrices while maintaining at least a 177°C (350°F)/wet service capability, and to get a prepreg that would process similarly to conventional epoxies. The ultimate target was room temperature mechanical performance and toughness of state-of-the-art epoxies and bismaleimides. The second target was to extend the hot/wet performance to 232°C (450°F) while maintaining these other features.

Cyanamid has developed a resin screening technique which is well suited to the current problem in which material quantities were limited. In Task I, emphasis was placed on the measurement of mechanical properties of the neat resin. Since good correla-

TABLE 2.5

EFFECT OF CURE CYCLE ON WATER ABSORPTION IN m-ATS HEAT RESINS

Formulation	Time (days) 0.3	1	4	5	8	11	14
m-ATS by Cyanamid cure (% H_2O gain)	1.17	1.40	1.54	1.55	1.55	1.57	1.65
m-ATS by AF cure (% H_2O gain)	1.19	1.75	1.97	2.09	2.14	2.17	2.20
m-ATS by Cyanamid cure with 300°C postcure (% gain)	1.02	1.33	1.43	1.43	1.43	1.43	1.49

tion had been found in previous work between matrix-dominated composite properties and neat resin properties.

2.2.1 Preliminary Screening

Because of the limited amount of m-ATB resin available for Tasks I to III, a set of preliminary screening tests were selected. They included dynamic mechanical analysis (DMA), flexural modulus of hot/wet conditioned samples, shrinkage and out-time evaluations. Figure 2.11 shows this screen schematically. All these tests were performed on a two gram sample of the formulated resin. The results of the tests were then compared to a a set of target values shown in Table 2.6.

The castings were made by pouring the resin into a preheated glass mold coated with Freekote 44 mold release agent. The castings were all cured using the shorter cycle desribed in Section 2.1.

Results of Preliminary Screening

The results of the prescreening evaluations for 53 formulations are shown in Table 2.7. Data on m-ATB and epoxy and BMI resins are presented in Table 2.1. Frequently, the dry glass transition temperature of the m-ATB formulations was equal to or higher than the m-ATB resin itself. The dry room temperature modulus of the formulated m-ATB was also improved over m-ATB. In most cases, the weight change after aging at 177°C (350°F) and 232°C (450°F) was less than 3%, well within the target regime. None of the formulated systems showed degradation in modulus or appearance after aging at 177°C (350°F) or 232°C (450°F). All formulations had out times longer than 30 days and many had out times of over 45 days. Details of the out time measurement and the appearance evaluation are given in the Appendix. The results of the out time measurements are also shown in Table 2.7. In most cases the aged coupon became slightly darker in color but showed

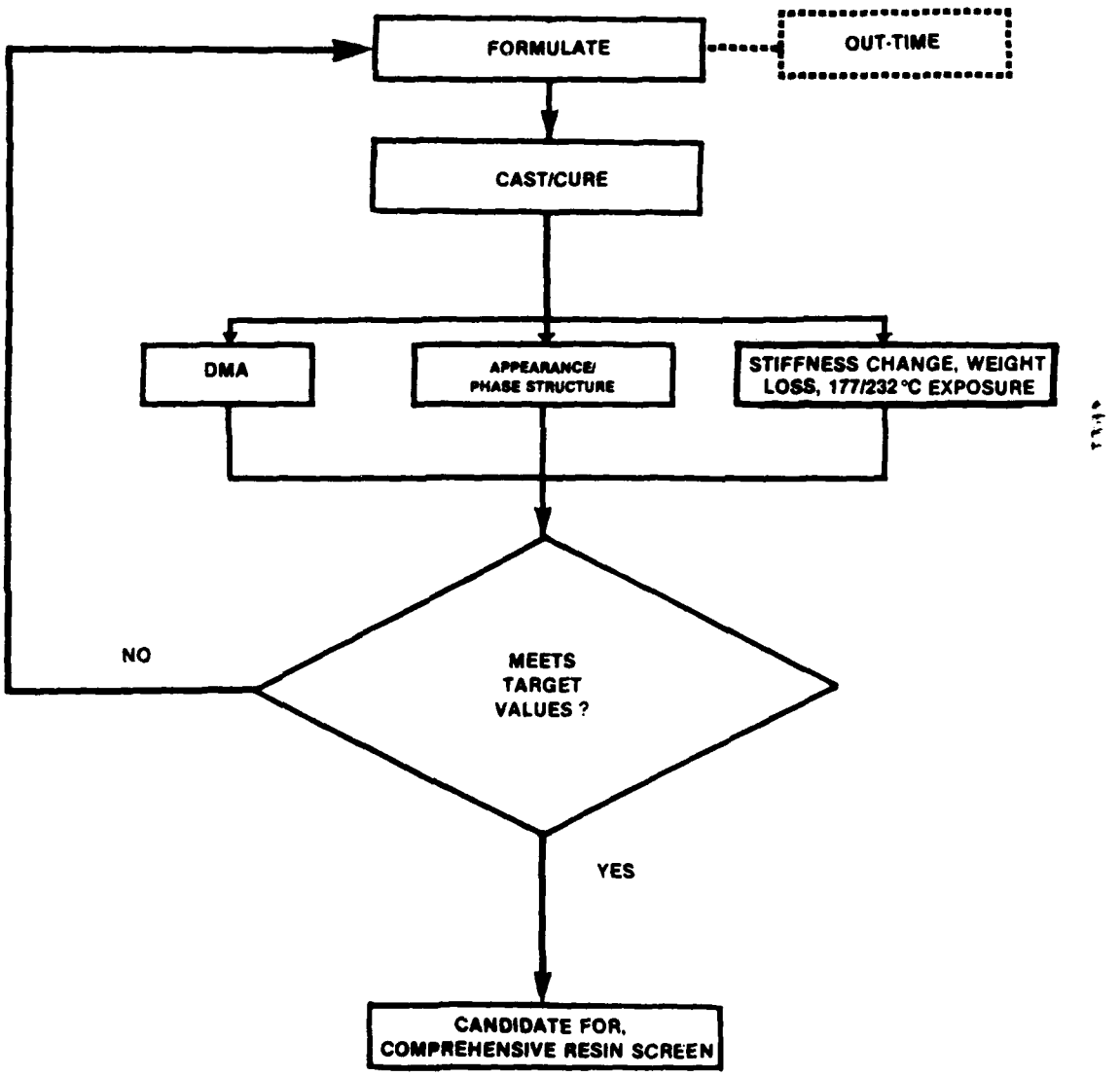


FIGURE 2.11 PRELIMINARY NEAT RESIN SCREEN
AT RESIN FORMULATIONS

TABLE 2.6

Target Values for Preliminary Neat Resin Screen

1) Glass Transition Temperature

   Tg, Modulus Intersept 204 - 260°C (400 - 500°F)
   Tg, Tan Delta 232 - 288°C (450 - 550°F)

2) Retension of Room Temperature Flex Modulus After Conditioning

   85-110% After 2 weeks @ 177°C (350°F)
   80-120% After Additional 30 hrs @ 232°C (450°F)

3) Weight Loss

   < 3% after 30 Hrs. at 232°C (450F)

4) Appearance/Phase Structure

   No major color change after aging, second phase compatability after aging

TABLE 2.7

DATA FOR m-ATB PRELIMINARY SCREEN FORMULATIONS

FORMULATION #	NOTEBOOK #	DMA TG (°C) TAN DELTA	DMA TG (°C) MOD. INT.	DMA TG (°C) 5 % OFFSET	FLEX MODULUS/GPa (MSI) RT	FLEX MODULUS/GPa (MSI) 350°F AGED	FLEX MODULUS/GPa (MSI) 450°F AGED	COMMENTS
1) CATB-1	S15168-145-1	365	347	286	3.62 (0.526)	4.35 (0.631)	4.17 (0.605)	Single phase, clear dark brown casting, no voids Out time >30 days, No discoloration after aging
2) CATB-2	S15168-145-2	354	334	273	3.78 (0.550)	4.10 (0.595)	4.17 (0.605)	Single phase, clear dark brown casting, no voids Out time >30 days, No discoloration after aging
3) CATB-3	S15168-145-3	347	326	266	3.98 (0.578)	3.96 (0.575)	4.07 (0.591)	Single phase, clear dark brown casting, no voids Out time >30 days, No discoloration after aging
4) CATB-4	S15168-148-2	343	284	266	4.26 (0.618)	4.28 (0.622)	4.44 (0.645)	Single phase, clear dark brown casting, no voids Out time >30 days, No discoloration after aging
5) CATB-5	S15168-159-1	-	-	-	-	-	-	Voids and cracks, not tested
6) CATB-6	S15168-159-2	-	-	-	-	-	-	Voids and cracks, not tested
7) CATB-7	S15168-165-1A	-	-	-	-	-	-	Incompatiable, gross phase separation, did not cast.
8) CATB-8	S15168-165-1	268	228	195	4.11 (0.597)	4.01 (0.582)	4.27 (0.620)	Single phase, clear dark brown casting, no voids Out time >45 days, No discoloration after aging
9) CATB-9	S15168-165-2	281	256	216	4.17 (0.605)	4.08 (0.592)	4.12 (0.598)	Single phase, clear dark brown casting, no voids Out time >45 days, No discoloration after aging
10) CATB-10	S15168-165-3	274	223	194	4.14 (0.601)	-	-	Single phase, clear dark brown casting, no voids Out time >45 days, No discoloration after aging
11) CATB-11	S15168-165-4	310	274	246	4.36 (0.633)	4.12 (0.598)	4.33 (0.628)	Single phase, clear dark brown casting, no voids Out time >45 days, No discoloration after aging
12) CATB-12	S15168-169-1A	-	-	-	-	-	-	Incompatiable, gross phase separation, did not cast
13) CATB-13	S15168-169-1	213	178	186	3.86 (0.561)	4.23 (0.614)	4.26 (0.618)	Dark brown, clear single phase casting no voids Out time >45 days, discoloration at fractured edges after aging

TABLE 2.7

DATA FOR m-ATB PRELIMINARY SCREEN FORMULATIONS - CON'T

FORMULATION #	NOTEBOOK #	DMA TG (°C) TAN DELTA	DMA TG (°C) MOD. INT.	DMA TG (°C) 5 % OFFSET	FLEX MODULUS/GPa (MSI) RT	FLEX MODULUS/GPa (MSI) 350°F AGED	FLEX MODULUS/GPa (MSI) 450°F AGED	COMMENTS
14) CATB-14	S15168-169-2	230	197	209	3.78 (0.546)	4.11 (0.596)	4.14 (0.601)	Dark brown opaque casting, phase separation, no voids. Out time >45 days, broken edges disclore after aging.
15) CATB-15	S15168-169-3	352	284	270	3.93 (0.570)	4.26 (0.618)	4.40 (0.639)	Clear dark brown casting, single phase no voids Out time >30 days, No discoloration after aging
16) CATB-16	S15168-169-4	313	259	246	3.86 (0.560)	4.21 (0.611)	4.15 (0.603)	Clear dark brown casting, single phase no voids Out time >45 days, No discoloration after aging
17) CATB-17	S15168-158-2A	-	-	-	-	-	-	Incompatiable mixture, could no be cast
18) CATB-18	S15168-158-2	298	242	215	3.95 (0.573)	4.05 (0.588)	3.84 (0.558)	Clear, single phase dark brown casting No voids. Out time appr. 30 days, no discoloration after aging.
19) CATB-19	S15168-171-1	320	260	240	4.07 (0.591)	3.93 (0.570)	4.33 (0.628)	Clear, single phase dark brown casting No voids. Out time >45 days, no discoloration.
20) CATB-20	S15168-171-2	268	226	223	3.86 (0.560)	3.88 (0.563)	4.13 (0.600)	Clear, single phase dark brown casting No voids. Out time >40 days, no discloration.
21) CATB-21	S15168-171-3	317	257	243	3.86 (0.560)	4.27 (0.620)	4.31 (0.625)	Clear, single phase dark brown casting No voids. Out time >40 days, no discloration.
22) CATB-22	S15168-171-4	296	259	233	3.65 (0.530)	3.89 (0.565)	4.18 (0.607)	Clear, single phase dark brown casting No voids. Out time appr. 30 days, no discoloration.
23) CATB-23	S15168-172-1	301	247	223	3.98 (0.578)	3.86 (0.561)	4.25 (0.617)	Clear, single phase dark brown casting No voids. Out time appr. 30 days, no discoloration
24) CATB-24	S15168-172-2A	-	-	-	-	-	-	Not compatiable, did not cast
25) CATB-25	S15168-172-3	248	199	178	4.04 (0.587)	3.69 (0.535)	4.28 (0.621)	Single phase, dark brown casting, no voids. Out time >40 days. No discoloration.

TABLE 2.7

DATA FOR m-ATB PRELIMINARY SCREEN FORMULATIONS - CON'T

FORMULATION #	NOTEBOOK #	DMA TG(°C) TAN DELTA	DMA TG(°C) MOD. INT.	DMA TG(°C) 5 % OFFSET	FLEX MODULUS/GPa (MSI) RT	FLEX MODULUS/GPa (MSI) 350°F AGED	FLEX MODULUS/GPa (MSI) 450°F AGED	COMMENTS
26) CATB-26	S15168-172-4	335	278	288	3.74 (0.543)	4.13 (0.600)	4.31 (0.625)	Single phase dark brown casting no voids. No discoloration.
27) CATB-27	S15168-175-1	223	185	160	3.60 (0.523)	3.24 (0.471)	3.77 (0.547)	Bubbles and small cracks in the casting
28) CATB-28	S15168-175-2	-	-	-	-	-	-	Incompatiable mixture, could not be cast
29) CATB-29	S15168-175-3	253	243	224	4.07 (0.591)	3.45 (0.501)	4.20 (0.610)	Some insoluble particles in the cured plaque
30) CATB-30	S15168-175-4	266	231	204	4.17 (0.605)	3.86 (0.561)	4.22 (0.612)	Single phase dark brown casting, no voids
31) CATB-31	S15168-181-1	276	246	236	4.24 (0.616)	- -	- -	Casting, no voids
32) CATB-32	S15168-181-2	315	275	281	4.30 (0.624)	- -	- -	Single phase, dark brown casting, no voids
33) CATB-33	S15168-185-1	272	249	220	3.40 (0.493)	3.20 (0.465)	4.97 (.721)	Single phase, dark brown casting, no voids
34) CATB-34	S15168-185-2	222	158	155	3.86 (0.561)	2.94 (0.427)	4.09 (.595)	Single phase, dark brown casting, no voids
35) CATB-35	S15168-185-3	269	239	218	3.44 (0.599)	3.32 (0.482)	4.92 (.714)	Phase separation in the cured plaque
36) CATB-36	S151680192-1	240	213	190	4.06 (0.590)	-	-	Single phase, clear, dark brown casting, no voids. Out time >30 days.
37) CATB-37	S15168-192-2	283	254	237	4.30 (0.624)	-	-	Single phase, clear, dark brown casting, no Out time >30 days.
39) CATB-39	S-15401	283	254	244	4.17 (0.605)	-		
40) CATB-40	S15401-28-1	269	229	207	4.17 (0.605)	-	-	Clear, light brown casting, no voids, single phase.

TABLE 2.7

DATA FOR m-ATB PRELIMINARY SCREEN FORMULATIONS - CONCLUDED

FORMULATION #	NOTEBOOK #	DMA TG (°C) TAN DELTA	DMA TG (°C) MOD. INT.	DMA TG (°C) 5 % OFFSET	FLEX MODULUS/GPa (MSI) RT	FLEX MODULUS/GPa (MSI) 350°F AGED	FLEX MODULUS/GPa (MSI) 450°F AGED	COMMENTS
41) CATB-41	S15401-28-2	285	267	254	3.43 (0.497)	-	-	Light brown casting, inhomogeneous, no void.
42) CATB-42	S15401-28-3	270	235	224	3.74 (0.542)	-	-	Clear light brown casting, single phase, no voids.
43) CATB-43	S15401-29-1	310	244	220	3.93 (0.570)	-	-	Clear light brown casting, homogeneous no voids.
44) CATB-44	S15401-31-1	286	265	253	3.99 (0.579)	-	-	Clear light brown casting, homogeneous no voids.
45) CATB-45	S15401-31-2	287	262	249	4.21 (0.610)	-	-	Opaque, dark green casting, no voids.
46) CATB-46	S15401-47-1	265	221	215	4.17 (0.604)	-	-	Dark brown casting, no voids.
47) CATB-47	S15401-47-2	201	172	159	3.45 (0.500)	-	-	Light brown casting, inhomogeneous two base structure.
48) CATB-48	S15401-47-3	229	203	186	4.17 (0.605)	-	-	Black casting, homogeneous, no voids.
49) CATB-49	S15401-53-1	274	246	215	4.15 (0.601)	-	-	Light brown casting, inhomogeneous, no voids.
50) CATB-50	S15401-63-4	242	216	198	4.37 (0.633)	-	-	Black casting, no voids.
51) CATB-51	S15401-63-1	296	272	254	4.22 (0.612)	-	-	Dark brown casting, no voids, homogeneous.
52) CATB-52	S15401-63-2	274	256	221	4.28 (0.620)	-	-	Dark brown casting, no voids, homogeneous.
53) CATB-53	S15401-63-3	273	248	207	4.55 (0.660)	-	-	Dark brown casting, no voids, homogeneous.
54) m-ATB		276	249	200	3.69 (0.535)			

no cracking or discoloration. In a few cases the fractured surfaces appeared discolored (dark yellow in color); however, the remaining edges did not show any discoloration. While quantitative evaluations of resin shrinkage during cure were not made, subjective observations concluded that there was less shrinkage in the m-ATB formulations compared to the unmodified m-ATB resin.

2.2.2 Comprehensive Screening

The data from the preliminary screen were compared in order to select formulations for the comprehensive screening. The number of formulations that met or exceeded the preliminary screening targets was too large to allow evaluation of all of them. Consequently, out of the formulations which met or exceeded the target properties, 18 formulations were selected to encompass a range of properties and a variety of features such as a) single phase vs. two phase morphology, b) different chemistry and c) different concentration levels of reactive modifiers or of m-ATB.

A summary of tests and test specimens used in the comprehensive resin screen is shown in Table 2.8 and the comprehensive neat resin screen is shown in Figure 2.12. Target values for the comprehensive screen are given in Table 2.9.

Results

The results of the comprehensive resin screen include the thermal analysis of cure, rheology of cure, flexural test data at room and elevated temperatures, dynamic mechanical analysis of glass transition temperature, and finally, the fracture toughness of the formulations.

TABLE 2.8

SUMMARY OF TESTS USED IN COMPREHENSIVE RESIN SCREENING PROGRAM

TEST	ASTM METHOD	SPECIMEN SIZE	TEST CONDITIONS	# OF TESTS
Heat of Polymerization, Exotherm (Before Cure)	DSC	10 mg.	Heating Rate = 10°C/min	1
Rheology	Rheometrics	Plates = 50mm dia.	Heating Rate = 2°C/min Gap = 1mm	1
Flexural Modulus, Strength, and Strain	D790	12.5mm x 41mm x 6mm	Dry, 23°C Wet, 177°C Wet, 232°C Dry, 232°C (Aged)	5 5 5 5
Dynamic Mechanical Analysis	D4056	12.5mm x 41mm x 6mm	Dry Wet	1 1
Compact Tensile*	E399	37.5mm x 41mm x 6mm	Dry, 73°F	5

* Two phase systems only

NOTE: Wet Conditioning - 2 weeks in water at 71°C (160°F)

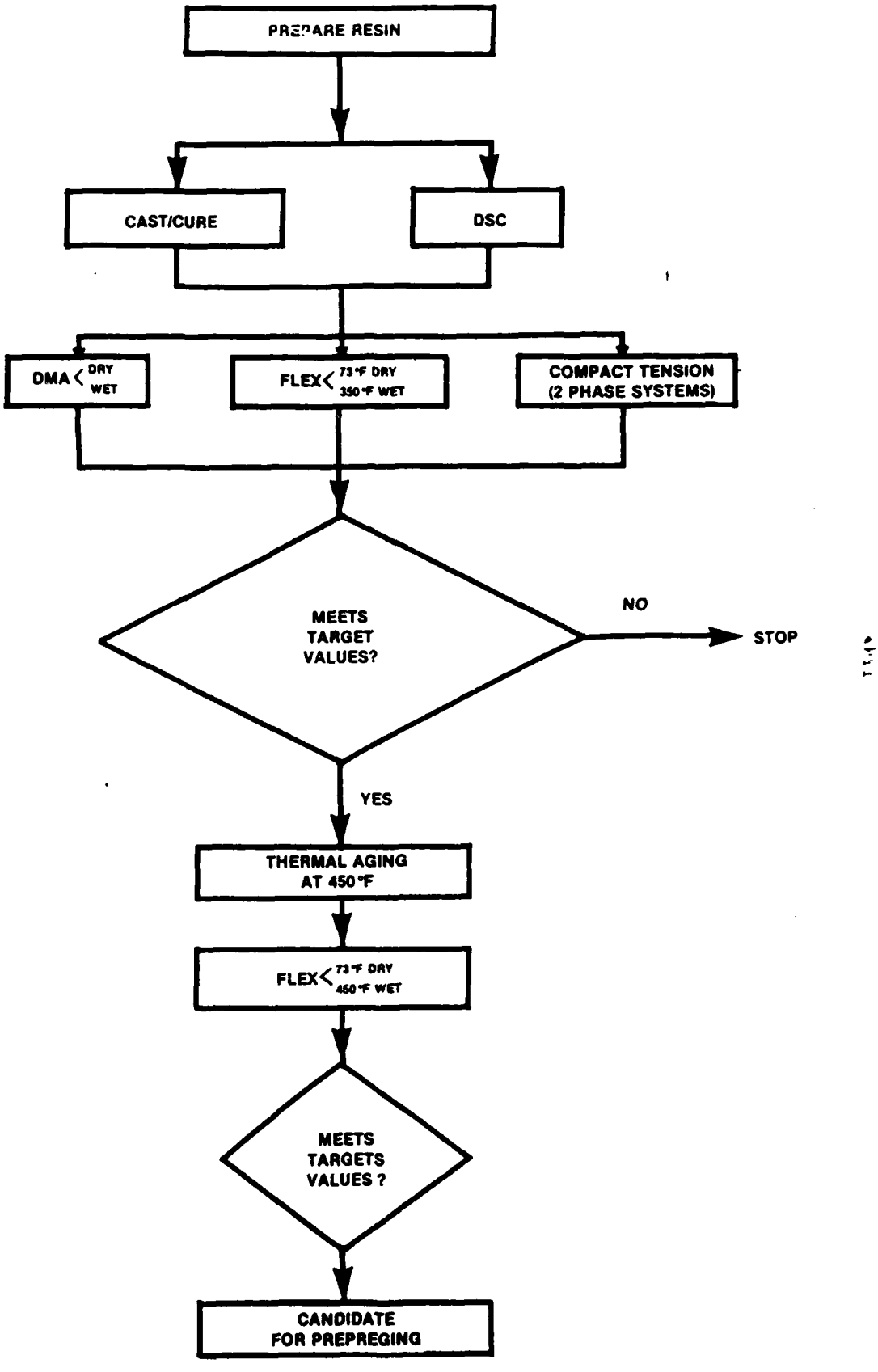


FIGURE 2.12 COMPREHENSIVE NEAT RESIN SCREEN AT RESIN FORMULATIONS

TABLE 2.9

Comprehensive Resin Screen - Initial Target Values

DMA 204-260°C (400-500°F) (Modulus Intersect)
232-288°C (450-550°F) (Tan Delta)

Compact Tension 175 J/m^2 (1 in-lb/in^2) (Two Phase Systems Only)

Flexural Stress-Strain Properties

Test Condition	Modulus GPa (MSI)	Target I Strength MPa (KSI)	Target I Strain %	Target II Strength MPa (KSI)	Target II Strain %
23°C (73°F/Dry)	3.79 (.550)	103 (15.0)	2.5	140 (20.0)	4.5
177°C (350°F/Wet)	2.24 (.325)	55 (8.0)	2.0	83 (12.0)	3.0
232°C (450°F/Dry Aged)*	2.24 (.325)	55 (8.0)	2.0	83 (12.0)	3.0
232°C (450°F/Wet)	2.24 (.325)	55 (8.0)	2.0	83 (12.0)	3.0

*Aged 30 hours @ 232°C (450°F)

DSC Characterization

The DSC analyses of m-ATB comprehensive screen formulations are shown in Table 2.10. Heats of polymerization of the formulated systems were lower than the pure m-ATB system. In most cases, a single symmetric peak was observed with a maximum between 240-276°C. In the case of CATB-39, CATB-44 and CATB-49, two peaks were observed, the smaller peak having a maximum at approximately 140°C in all three cases.

Rheological Analysis

Results from Rheometrics rheological profiles on m-ATB formulated systems are shown in Table 2.11. At 70°C, the common prepregging temperature, all of the formulations had a higher viscosity than the m-ATB control ranging from 7.3 poise for m-ATB itself to 11,900 P for CATB-49. The minimum viscosity ranged from 0.2 for m-ATB to 7.7 poise for CATB-48. In most of the systems, the minimum occurred between 160-175°C with a sharp increase in viscosity above that temperature. The temperature vs. viscosity profiles on CATB-44, CATB-49 and CATB-52 are shown in Figures 2.13 through 2.15.

Flexural Stress-Strain and Dynamic Mechanical Analysis

The flexural properties of the comprehensive resin screen formulations are listed in Table 2.12. Also included are the Tg's determined by dynamic mechanical analysis (DMA) and water absorption after 2 weeks immersion in distilled water.

Formulation CATB-32 showed the highest 232°C (450°F)/wet modulus but had poor strength and strain to failure. CATB-44 showed a good combination of properties with a strain to failure of about 3.5% and a 177°C (350°F)/wet modulus of about 0.45 MSI. All formulations except CATB-47 exceeded our target modulus of 0.325 MSI at 177°C (350°F)/wet.

TABLE 2.10

DSC ANALYSIS OF AT RESIN FORMULATIONS

CATB #	Exotherm Onset Temp, °C	Exotherm Peak Temp, °C	Exotherm Completion Temp, °C	Heat of Polymerization Cal/g
m-ATB	155	241	308	134
CATB-4	171	252	305	75
CATB-11	172	258	326	85
CATB-31	162	244	293	75
CATB-32	122	234	309	111
CATB-36	195	261	308	84
CATB-37	182	241	300	70
CATB-39	88	264	330	61
CATB-43	159	249	318	60
CATB-44	103	263	334	67
CATB-45	164	259	330	69
CATB-46	154	276	336	62
CATB-47	106	260	316	52
CATB-48	133	271	312	103
CATB-49	185	264	334	65
CATB-50	169	268	312	137
CATB-51	184	261	334	72
CATB-52	166	261	369	99
CATB-53	169	264	375	102

(Heating Rate = 10°C/min)

TABLE 2.11

RHEOLOGICAL BEHAVIOR OF AT RESIN FORMULATIONS

Resin System	Viscosity at 70°C (Poise)	Minimum Viscosity [Poise (T °C)]	Viscosity Increse After Minimum*
m-ATB control	7.3	0.2 (145-190)	Medium
CATB-4	390	0.6 (159)	Medium
CATB-11	49	0.2 (167)	Sharp
CATB-31	240	0.6 (166)	Sharp
CATB-32	52	0.3 (160)	Medium
CATB-36	261	0.8 (173)	Medium
CATB-37	687	1.4 (161)	Sharp
CATB-43	56	0.3 (161)	Sharp
CATB-41	2493	9 (163)	Sharp
CATB-45	459	3 (162)	Sharp
CATB-45 (Repeat)	605	2.2 (157)	Sharp
CATB-46	1814	5.2 (160-200)	Sharp
CATB-47	12.6	0.2 (171)	Sharp
CATB-48	850	7.7 (143-168)	Sharp
CATB-49	11860	4.4 (162)	Medium
CATB-50	601	1.6 (178)	Sharp
CATB-51	454	1.4 (160)	Sharp
CATB-52	927	3.3 (163)	Sharp
CATB-53	976	5.5 (161)	Sharp

* Gradual = Viscosity increase of at least one decade over thirty degrees or more after minimum viscosity

Medium = Viscosity increase of at least one decade over twenty to thirty degrees after minimum viscosity

Sharp = Viscosity increase of at least one decade over twenty degrees or less after minimum viscosity

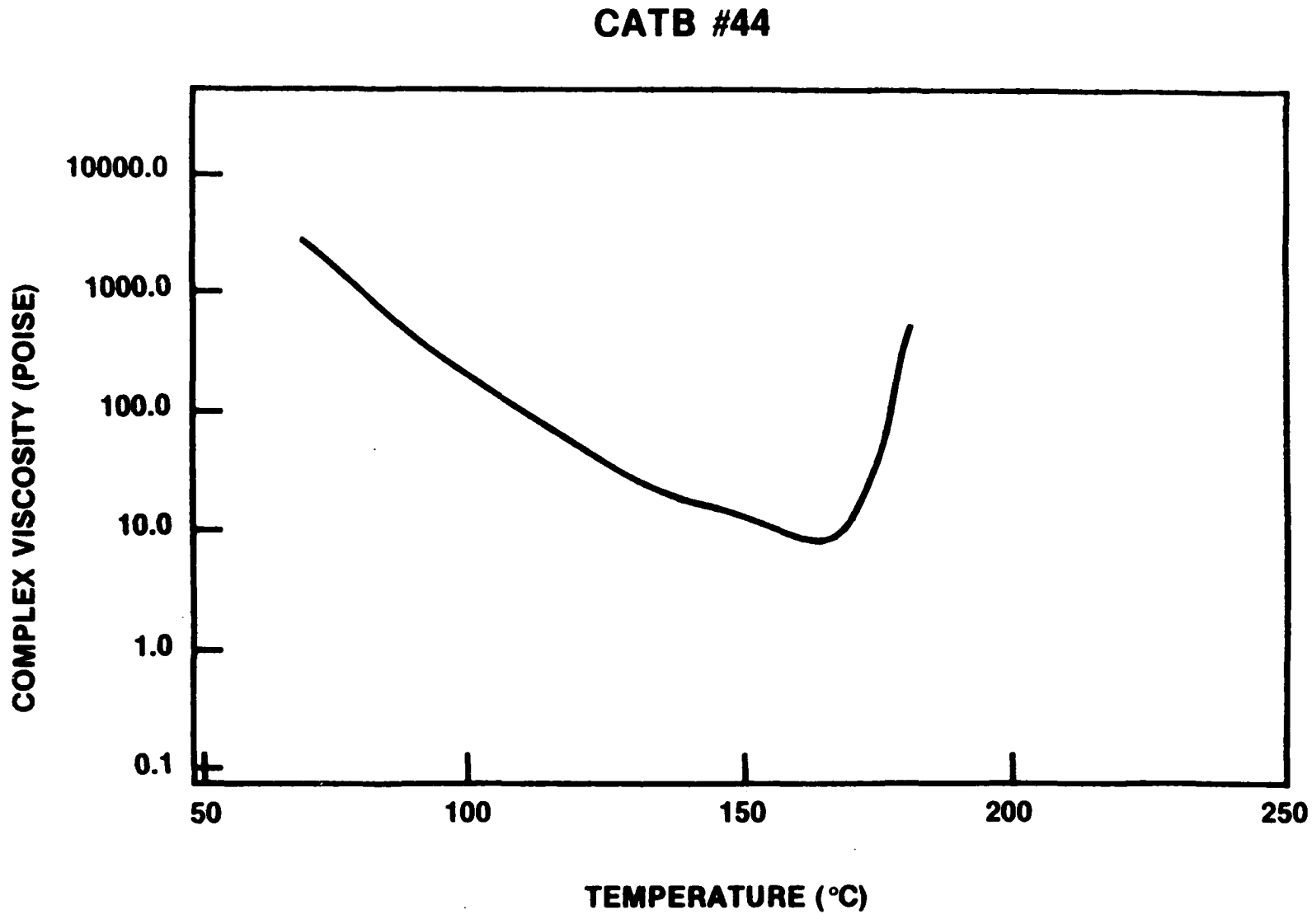


FIGURE 2.13
RHEOLOGICAL PROFILE OF CATB-44

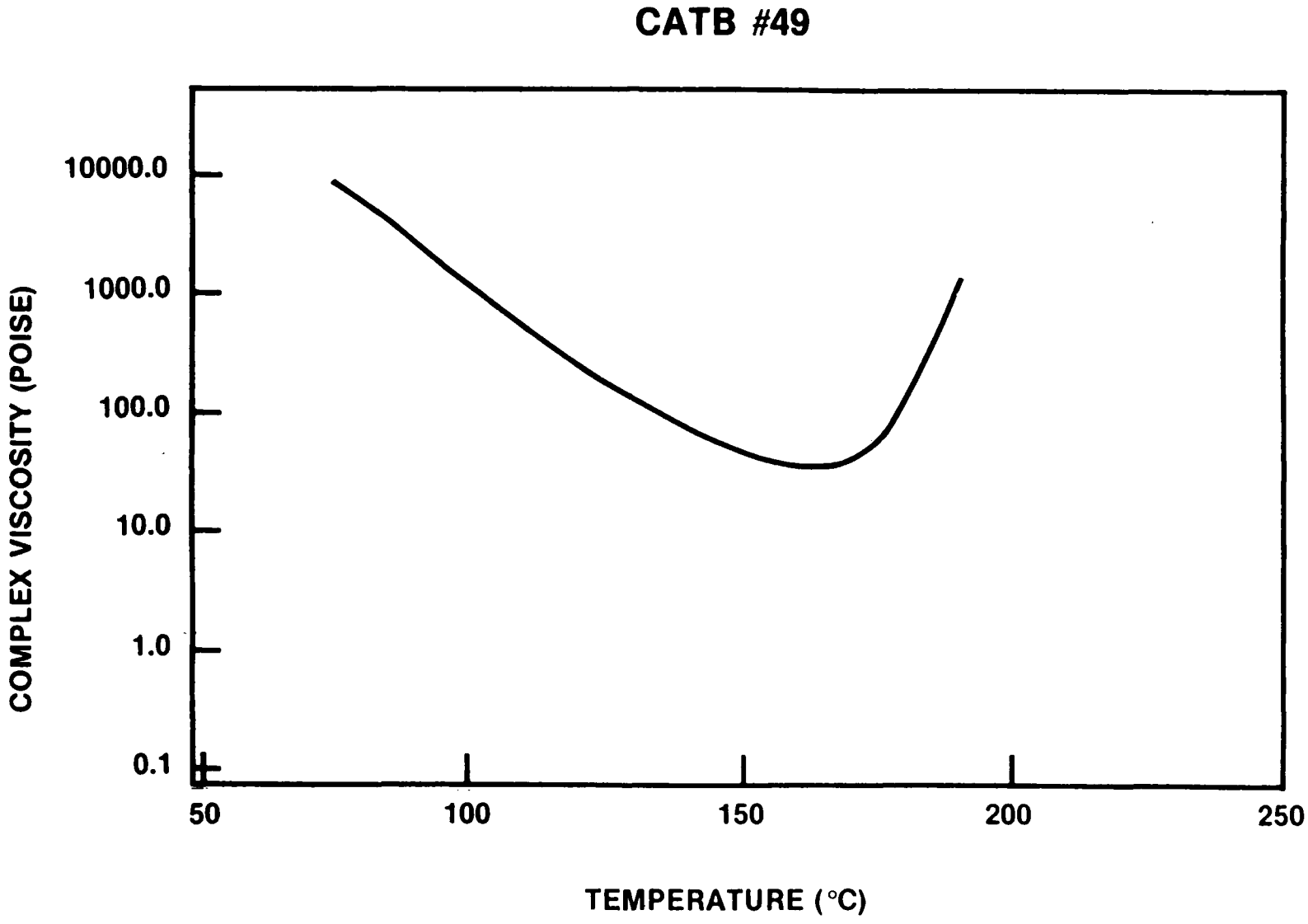


FIGURE 2.14
RHEOLOGICAL PROFILE OF CATB-49

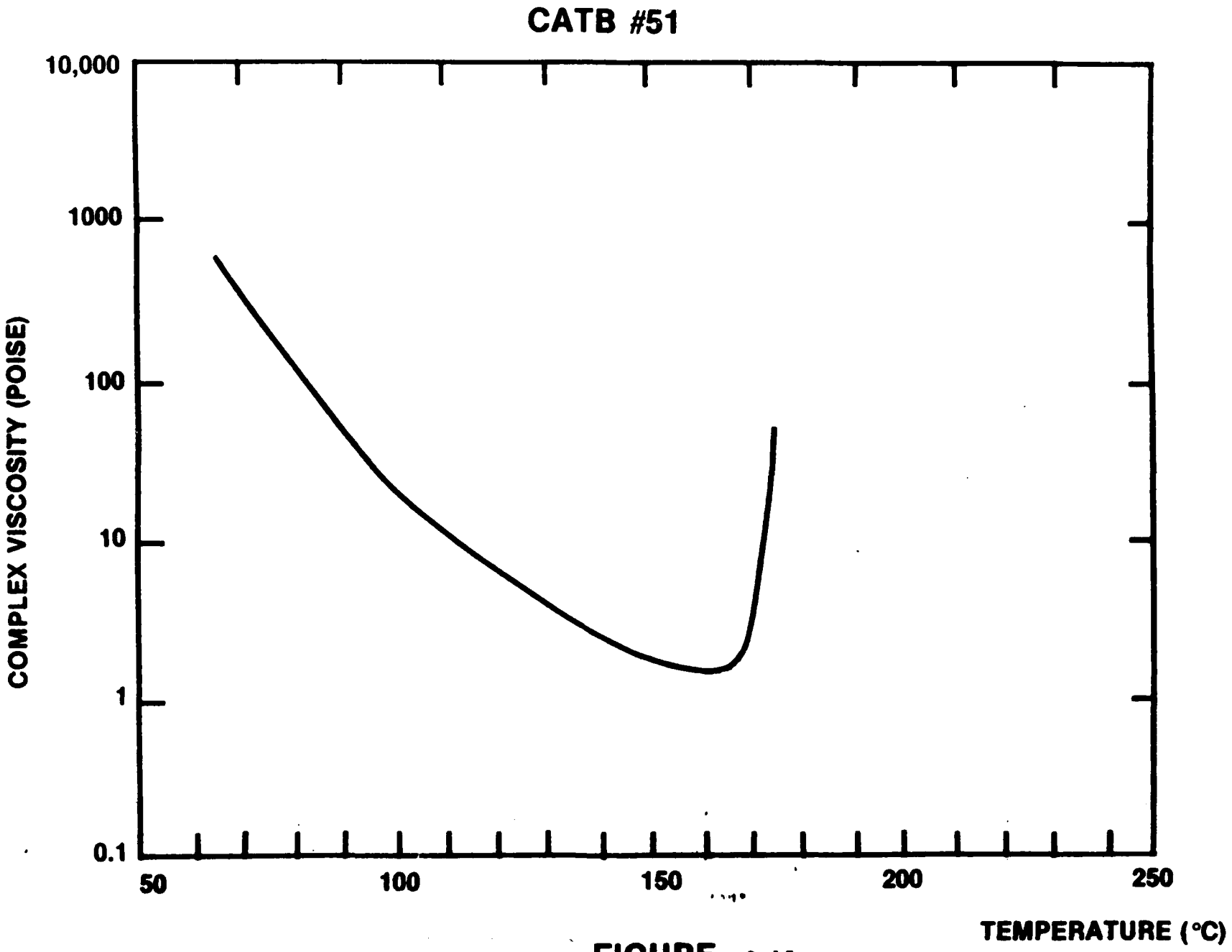


FIGURE 2.15
RHEOLOGICAL PROFILE OF CATB-51

TABLE 2.12

COMPREHENSIVE NEAT RESIN EVALUATION - m-ATB SYSTEMS

Formulation Identification	Test Condition	Tg, °C	Modulus GPa	(MSI)	Strength MPa	(KSI)	Strain %	Work-to-Break MJ/m^3	(in-lbs/in^3)	Water Absorption %	G_{IC} J/m^2	G_{IC} $in\text{-}lb/in^2$
m-ATB (Cyanamid Cure	23°C/Dry	276	3.69 ±.01	(.535± .001)	90.2 ± 3.4	(13.1 ±0.5)	2.5 ±0.1	1.38 ± .10	(200±15)	—	75	0.43
	177°C/Wet	272	2.79 ±.04	(.405± .006)	79.2 ±5.5	(11.5 ± .8)	3.0 ±.2	1.39 ±.21	(201±30)	0.23		
	204°C/Wet		2.1 ±.1	(.307± .011)	72 ±6	(10.4 ± .9	5.9 ±1.8					
	232°C/Wet		1.4 ±.1	(.204 ±.018)	46 ±4	(6.6 ±.6	6.1 ±1.5					
CATB-4	23°C/Dry	321	4.39 ±.04	(.638± .006)	110 ±9.6	(16.1 ±1.4)	2.5 ±0.2	1.52 ± .27	(220±40	—		
	177°C/Wet	328	2.47 ± .09	(.359± .014)	47 ±8.3	(6.9 ±1.2)	1.9 ±0.3	1.21 ± .03	(175±55)	3.47		
	232°C/Wet		1.61 ±.03	(.234 ±.005)	38.6 ±6.2	(5.6 ±0.9	2.6 ±0.5					
CATB-11	23°C/Dry	307	4.15 ± .06	(.603± .008)	116 ±9.6	(16.8 ±1.4)	2.8 ±0.3	1.76 ± .34	(256±50)	—	79	0.45
	177°C/Wet	288	2.43 ± .05	(.353± .007)	55 ±7.6	(8.0 ±1.1)	2.2 ±0.4	1.52 ± .52	(220±75)	2.69		
	232°C Wet		1.62 ±.03	(.236 ±.005)	39.3 ±6.2	5.7 ±0.9	2.5 ±0.5					
CATB-31	23°C/Dry	276	4.24 ±.04	(.616± .006)	109 ±1.3	(15.8 ±1.9	2.6 ±0.3	1.39 ±.29	(202±51)	—	82	0.47
	177°C/Wet	274	2.77 ±.09	(.402± .013)	83.4 ±6.9	(12.1 ±1.0	3.2 ±0.3	1.52 ±.29	(220±42)	1.99		
	232°C/Wet		1.48 ±.04	(0.215 ± .006)	39.9 ±4.1	(5.8 ±0.6)	3.0 ±0.4					
CATB-32	23°C/Dry	315	4.30 ±.04	(.624± .006)	91.6 ±9.0	(13.3 ±1.3)	2.2 ±0.2	.99 ± .18	(143±26)	—	33	0.19
	177°C/Wet	315	2.87 ±.03	(.416± .005)	49.0 ±9.6	(7.2 ±1.4)	1.8 ±0.4	.52 ±/18	(75±26)	1.60		
	204°C/Wet		2.3 ±.1	(.341 ±.008)	50 ±3	(7.3 ± .4	2.2 ±0.1					
	232°C/Wet		1.89 ±.04	(.273 ±.006)	43 ±8	(6.2 ±1.2	2.3 ±0.4					

TABLE 2.12
COMPREHENSIVE NEAT RESIN EVALUATION - m-ATB SYSTEMS (CONTINUES)

Formulation Identification	Test Condition	Tg, °C	Modulus GPa	Modulus (MSI)	Strength MPa	Strength (KSI)	Strain %	Work-to-Break MJ/m^3	Work-to-Break (in-lbs/in^3)	Water Absorption %	G_{IC} J/m^2	G_{IC} in-lb/in^2
CATB-32 Repeat 1	23°C/Dry	339	4.2 +.1	(0.608 +.014)	74 +38	(10.7 +5.6)	1.8 +.9	0.78 +.76	(113±111)		33	0.19
	177°C/Wet		3.1 +.1	(.450 +.017)	56 +9	(8.1 +1.3)	1.8 +.4	0.53 +.19	(77±27)	1.32		
	232°C/Wet		2.0 ±.1	(.293 ±.012)	43 ±3	(6.2 ±.5)	2.2 ±.3					
CATB-32 Repeat 2	23°C/Dry		4.1	(.599)	102	(14.8)	2.7	1.49	(216)			
CATB-36	23°C/Dry	245	4.06 +.01	(.5900 .002)	107 +11	(15.6 +1.7)	2.6 ±0.3	1.57	(228±43)	—		
	177°C/Wet	240	2.78 +.03	(.403+ .005)	91.6 +20.7	(13.3 ±3.0)	3.6 ± .9	2.04 ± .92	(296±134)	0.94		
	232°C/Wet		<.34	(<.05)	Break		>10.					
CATB-37	23°C/Dry	285	4.30 +.02	(.624+ .003)	131 +11	(19.0 ± 1.6)	3.1 ±0.3	2.16 +/42	(313±61)	—	82	0.47
	177°C/Wet	283	2.54 +.17	(.369+ .025)	61.3 +10.3	(8.9 +1.5	2.5 +.4	0.89 ± .28	(129±41)	3.3		
	232°C/Wet		1.43 ±.11	(.208 ±.016)	43. ±.3	6.3 ±0.4)	3.5 ±0.4					
CATB-39	23°C/Dry	283	3.98 +.12	(.578+ .017)	159 +13	(23.1 +1.9)	4.1 ±0.4	3.38 +.65	(490±95)		1.75	1.00
	177°C/Wet	292	2.84 ±.12	(.413+ .018)	90 ±13	(13.0 ±1.9)	3.2 ±.4	1.5 ±.4	(223±60)	—		
CATB-43	23°C/Dry	233	7.5 +.03	(.570+ .005)	103 .005)	(15.0 +15	2.7 +2.2)	1.48 +.4	(215±69) +.48		72	0.41
	177°C/Wet	255	2.5 +.09	(.375+ .014)	65 +11	(9.4 +1.6)	2.5 +.4	.86 ±.26	(125±38)	2.33		
	204°C/Wet		2.1 +.1	(.306 +.015)	52 +1	(7.6 +1.1)	2.6 +4					
	232°C/Wet		1.7 ±.1	(.245 +.016)	99 ±4	(7.1 ±.6)	3.2 +.6					

TABLE 2.12

COMPREHENSIVE NEAT RESIN EVALUATION - m-ATB SYSTEMS (CONTINUES)

Formulation Identification	Test Condition	Tg, °C	Modulus GPa	Modulus (MSI)	Strength MPa	Strength (KSI)	Strain %	Work-to-Break MJ/m^3	Work-to-Break ($in\text{-}lbs/in^3$)	Water Absorption %	G_{IC} J/m^2	G_{IC} $in\text{-}lb/in^2$
CATB-44	23°C/Dry	286	3.99 +.02	(.579 +.003)	120 +18	(17.4 +2.6)	2.8 .7	2.06 +.69	(298±100)		161	0.92
	177°C/Wet	289	2.88 +.06	(.418+ .009)	81 +6	(11.7 +.8)	2.8 +.3	1.17 ±.21	(171±30)	2.58		
	232°C/Wet		1.7 ±.1	(.245 ±.016)	49 ±4	(7.1 ±.6	3.2 ±.6					
CATB-44 Repeat 1	23°C/Dry	296	4.3 ±.1	(0.625 ±.013)	136 ±26	(19.7 +3.8)	3.4 ±.8	2.57 ±1.20	(373±175)		101	0.63
	177°C/Wet		3.2 ±.4	(.462 ±.059)	89 ±11	(12.9 ±1.6)	2.9 ±.3	1.48 ±.03	(215±4.9)	1.83		
CATB-44 Repeat 2	23°C/Dry		4.2 ±.09	(.616 ±.013)	116 ±16	(16.8 ±2.3	2.8 ±.4	1.67 ±.46	(243±67)			
CATB-45	23°C/Dry	287	4.20 +.05	(.610 +.007)	132 +9	(19.2 +1.3)	3.4 +3.6	2.33	(339±52)		98	0.56
	177°C/Wet	294	3.03 +.08	(.440 +.012)	61 +12	(8.9 +1.8)	2.0 +.4	.66 +25)	(96±37)	2.79		
	204°C/Wet		1.4 +.1	(.270 +.009)	36 +10	(5.2 +.14)	2.1 +.6					
	232°C/Wet		1.7 ±.1	(.241 ±.016)	39 ±8	(5.7 +1/2)	2.6 ±.6				103	0.59
CATB-45 Repeat 1	23°C/Dry	290	4.7 +.1	(.685 +.015)	131 +7	(19.1 +1.0)	2.6 +.5	1.67	(243±83)			
	177°C/Wet		3.0 +.1	(.439 ±.010)	69 ±16	(10.0 +2.3)	2.4 ±.5	0.90 ±.42	(132±62)	2.32		
CATB-45 Repeat 2	23°C/Dry		4.4	(.637)	135	(19.6)	3.1	2.10	(306)		88	0.50
CATB-46	23°C/Dry	265	4.16 +.04	(.604 +.007)	124 +0.2	(18.0 +.03)	2.9 +2	1.90 +.31	(276±45)		61	0.35
	177°C/Wet		2.54 ±.07	(.369 ±.011)	65 ±10	(9.4 ±1.5)	2.6 +.6	0.91 ±.30	(132±43)	2.59		

TABLE 2.12
COMPREHENSIVE NEAT RESIN EVALUATION - m-ATB SYSTEMS (CONTINUES)

Formulation Identification	Test Condition	Tg, °C	Modulus GPa	Modulus (MSI)	Strength MPa	Strength (KSI)	Strain %	Work-to-Break MJ/m^3	Work-to-Break (in-lbs/in^3)	Water Absorption %	G_{IC} J/m^2	G_{IC} in-lb/in^2
CATB-47	23°C/Dry	201	3.44 ±.05	(.500 ±.008)	161 ±7	(23.4 ±1.0)	5.2 ±.4	4.46 ±.20	(647±30)		212	1.21
	177°C/Wet		0.95 ±.23	(.138 ±.034)	NB		>10	2.80 ±1.5	(407±212)	1.99		
CATB-48	23°C/Dry	229	4.17 ±.08	(.605 ±.011)	159 ±12	(23.1 ±1.7)	3.8 ±.4	3.15 ±.61	(457±88)		130	0.74
	177°C/Wet		2.25 ±.03	(.327 ±.005)	83 ±5	(12.1 ±.7)	7.3 ±.9	4.49 ±.85	(652±124)	2.67		
CATB-49	23°C/Dry	274	4.14 ±.06	(.601 ±.008)	145 ±16	(21.1 ±2.3)	3.5 ±.4	2.70 ±.61	(392±88)		165	0.94
	177°C/Wet		2.67 ±.06	(.388 ±.010)	85 ±9	(12.4 ±1.3)	3.7 ±0.4	1.65 ±.43	(240±63)	1.99		
	204°C/Wet		1.6 ±.3	(.234 ±.044)	44 ±8	(6.4 ±1.2)	4.5 ±.8					
	232°C/Wet		0.9 ±.1	(.127 ±.021)	33 ±2	(4.8 ±.3)	5.9 ±2.2					
CATB-49 Repeat 1	23°C/Dry	275	4.2 ±.03	(0.612 ±.005)	121 ±18	(17.5 ±2.6)	2.9 ±.5	1.78 ±.56	(259±82)		130	0.74
	177°C/Wet		2.7 ±.1	(.387 ±0.16)	90 ±12	(13.0 ±1.7)	3.8 ±.5	1.83 ±.61	(266±89)	1.99		
CATB-49 Repeat 2	23°C/Dry		4.5 ±.2	(.656 ±.028)	139 ±19	(20.2 ±2.7)	3.4 ±.5	2.43 ±.80	(354±116)		110	0.63
CATB-50	23°C/Dry	242	4.36).10	(.633 ±.015)	136 ±24	(19.7 ±3.5	2.8 ±.4	1.90 ±.39	(277±57)		82	0.47
	177°C/Wet		2.49 ±.24	(.362 ±.035)	91 ±4	(13.2 ±.6)	5.5 ±.9	3.12 ±.50	(453±72)	2.67		
	204°C/Wet	0.4	(0.063)		16	(2.3)	10.9					
	232°C/Wet		<0.1	<.022	NB		>10					
CATB-50 Repeat 1	23°C/Dry		4.4 ±.2	(.636 ±.036)	161 ±25	(23.4 ±3.7)	3.9 ±.9	3.3 ±.9	(476±134)		102	0.58

TABLE 2.12

COMPREHENSIVE NEAT RESIN EVALUATION - m-ATB SYSTEMS (CONCLUDED)

Formulation Identification	Test Condition	Tg, °C	Modulus GPa	(MSI)	Strength MPa	(KSI)	Strain %	Work-to-Break MJ/m^3	(in-lbs/in^3)	Water Absorption %	J/m^2	G_{IC} in-lb/in^2
CATB-51	23°C/Dry	296	4.21 ±.14	(.612 ±.021)	134 ±36	(19.5 ±5.3)	3.3 ±1.0	2.4 ±1.5	(351±217)		119	0.68
	177°C/Wet		2.94 ±.14	(.427 ±.021)	71 ±22	(10.3 ±3.2)	2.5 ±3.2	0.94 ±.7	(137±84)	2.55 ±0.57		
	204°C/Wet		1.7 ±.04	(.248 ±.006)	60 ±2	(7.2 ±.3)	3.2 ±.1					
	232°C/Wet		1.6 ±.1	(.237 ±.015)	48 ±1	(6.9 ±.1)	3.1 ±.1					
CATB-51 Repeat 1	23°C/Dry		4.4 ±.1	(.639 ±.012)	140 ±25	(20.4 +3.6)	3.4 ±.7	2.45 ±.97	(356+141)		116	0.66
CATB-52	23°C/Dry	274	4.27 ±.20	(.620 ±.029)	128 ±25	(18.6 ±3.7)	3.1 ±.7	2.07 ±.83	(301±121)		91	0.52
	177°C/Wet		2.73 ±.13	(.397 ±.019)	68 ±	(9.9 ±.01)	2.7 ±.2	.92 +0.4	(133±6)	1.81		
	204°C/Wet		1.6 +0.1	(.227 ±.008)	28 ±2	(5.5 ±.3)	2.7 ±.3					
	232°C/Wet		1.4 ±.1	(.197 ±.015)	22 ±3	(3.2 ±.3)	1.8 ±.3					
CATB-52 Repeat 1	23°C/Dry		4.4 ±.2	(.632 ±.029)	130 ±28	(18.9 +4.1)	3.1 ±.5	2.16 ±.71	(313±104)		126	0.72
CATB-53	23°C/Dry	273	4.54 ±.19	(.660 ±.027)	150 ±1	(21.7 ±.17)	3.6 ±.3	2.62 ±.08	(381±12)		110	0.63
	177°C/Wet		2.81 ±.08	(.409 ±.013)	79 ±19	(11.4 ±2.7)	3.2 ±.9	1.36 ±.66	(198±96)	1.98		
	204°C/Wet		1.6 ±.1	(.237 ±.018)	52 ±3	(7.5 ±.5	4.9 ±.4					
	232°C/Wet		2.0 ±.04	(.150 ±.007)	37 ±3	(5.4 ±.4)	4.4 ±1.2					
CATB-53	23°C/Dry		4.4	(.636)	127	(18.5)	2.9	1.82	(2.65)		110	0.63

Because of an increased emphasis from AFWAL on high temperature/wet properties, testing at 204°C and 232°C was carried out. The 204°C (400°F)/wet flexural properties on the eight systems selected for further evaluation are also included in Table 2.12. All these systems show a significant reduction in modulus when tested at 204°C (400°F) as compared to 177°C (350°F). Two systems, CATB-32 and CATB-44, show 204°C (400°F)/wet moduli greater than 0.3, but CATB-50 is less than 0.1 MSI. The rest of the systems are between 0.22 to 0.3 MSI.

The 232°C (450°F)/wet moduli on selected m-ATB formulations were required and are also included in Table 3.12. CATB-32 had the highest wet modulus at 232°C (450°F): 0.273 and 0.29 MSI CATB-44, -45, and -51 had moduli greater than m-ATB itself. State-of-the-art bismaleimides typically have a 232°C (450°F)/wet modulus of less than 0.20 MSI. In that respect CATB-32, -44, -45 are significantly better than the bismaleimide system.

Four formulations (CATB-32, -44, -45 and -49) were repeated to confirm the values obtained. The stress-strain and thermal properties in these systems are reasonably reproducible.

Generally, the glass transition temperatures shown in Table 3.12 were higher than the m-ATB resin alone. In addition, the shape of the tan delta curves were different than the control. The loss peaks for CATB-44, -49, and -51 were broader than the unmodified system. The increased breadth and different shape of the modulus and tan delta curves indicate that there may be significant differences in the network morphology that is formed in the various formulations.

Fracture Toughness

The fracture toughness of the full screen castings with two-phase structures were measured using a compact tension specimen. The results are shown in Table 2.12. The compact

tension fracture surfaces of CATB-32, -44, -49 and -51 were examined by scanning electron microscopy, and are shown in Figures 2.16 through 2.19 and can be compared to the fracture surface of m-ATB shown in Figure 2.20.

The fracture surface of m-ATB was smooth and lacked significant fracture features. This is consistent with its low fracture toughness, G_{IC} of 75 J/m^2 (0.43 in-lb/in^2).

CATB-32's fracture surface (Figure 2.16) has few fracture features indicative of toughening. This is consistent with its low toughness which is about the same as m-ATB's, i.e., 33 J/m^2 (0.19 in-lb/in^2).

Greater roughness in the fracture surface is seen in CATB-44, -49, and -51. CATB-51, shown in Figure 2.19, has spherical domains, about 2 microns in diameter. The domains are rougher than the continuous phase, and they cause some crack front deviation, thereby increasing the effective fracture surface area. This is consistent with CATB-51's higher toughness, 117 J/m^2 (0.67 in-lb/in^2).

Greater fracture surface roughness is seen in CATB-44 and -49, as shown in Figures 2.17 and 2.18. In both cases, a discontinuous, brittle phase is surrounded by a continuous, rougher phase. In CATB-44, the domains have a diameter of around 3 microns. The greater fracture surface roughness from this phase structure is reflected in the formulations' toughness. Both had G_{IC} of about 130 J/m^2 (0.76 in-lb/in^2).

2.2.3 Conclusions

The data from the comprehensive evaluation of the ATB formulations were compared by looking at the trade off between 177°C (350°F)/wet properties and toughness. This comparison is shown in Figure 2.21. Notice that CATB-44, -49 and -51 stand out in the

FIGURE

FRACTURE SURFACE OF CATB-32

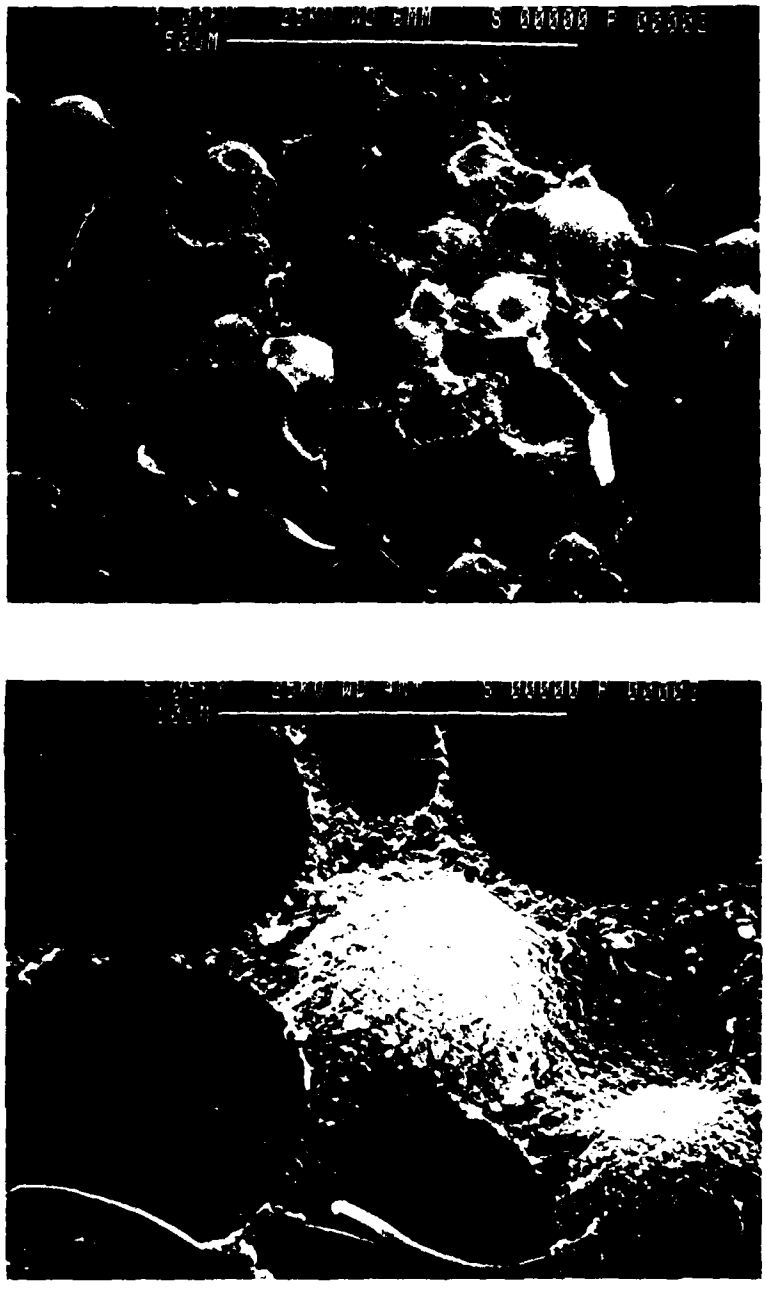
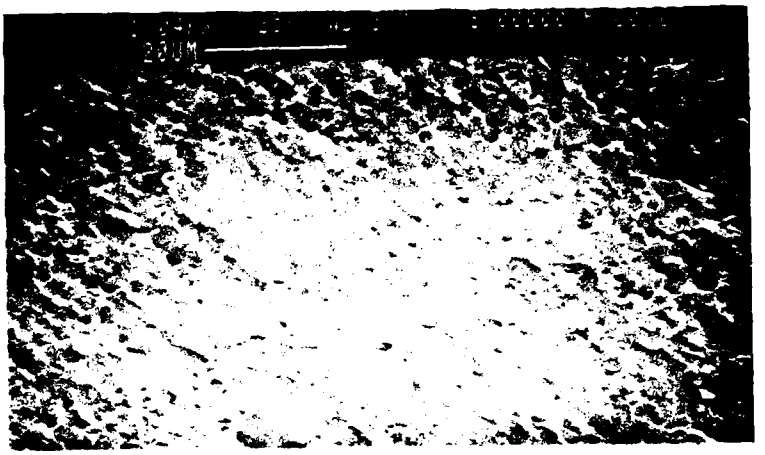


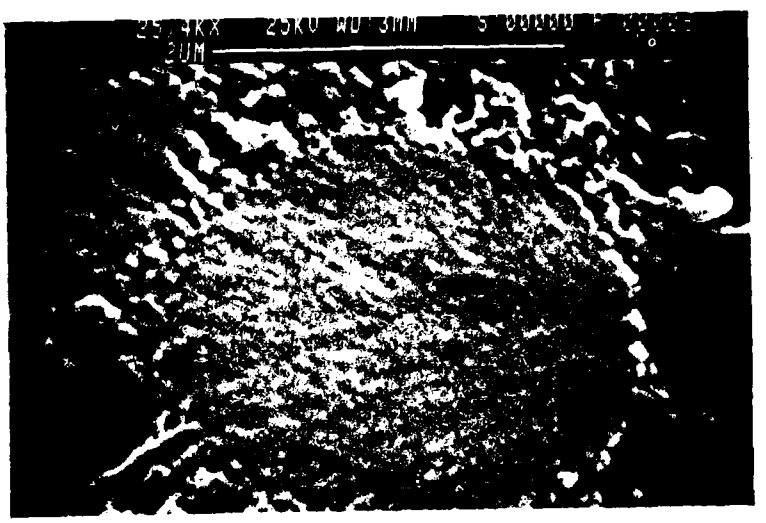
FIGURE 2.17

FRACTURE SURFACE OF CATB-44



a)

b)



c)

FIGURE 2.18

FRACTURE SURFACE OF CATB—49

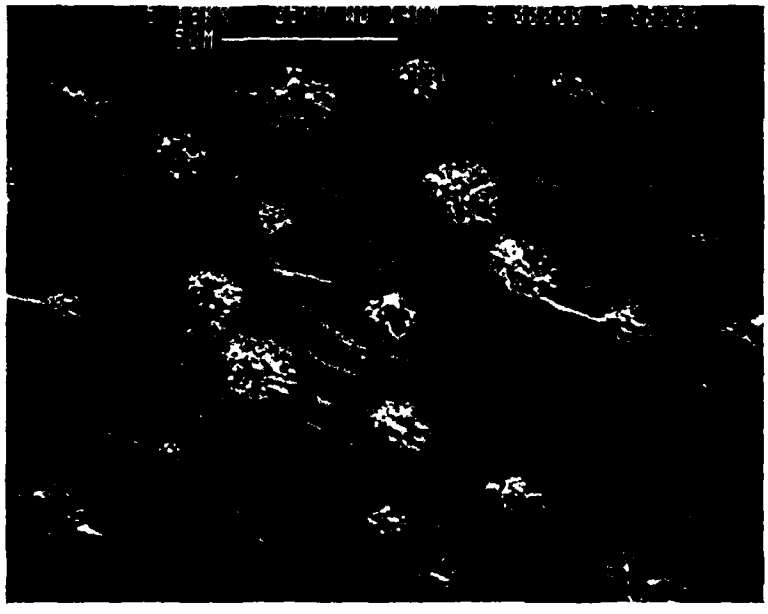


FIGURE 2.19

FRACTURE SURFACE OF CATB-51

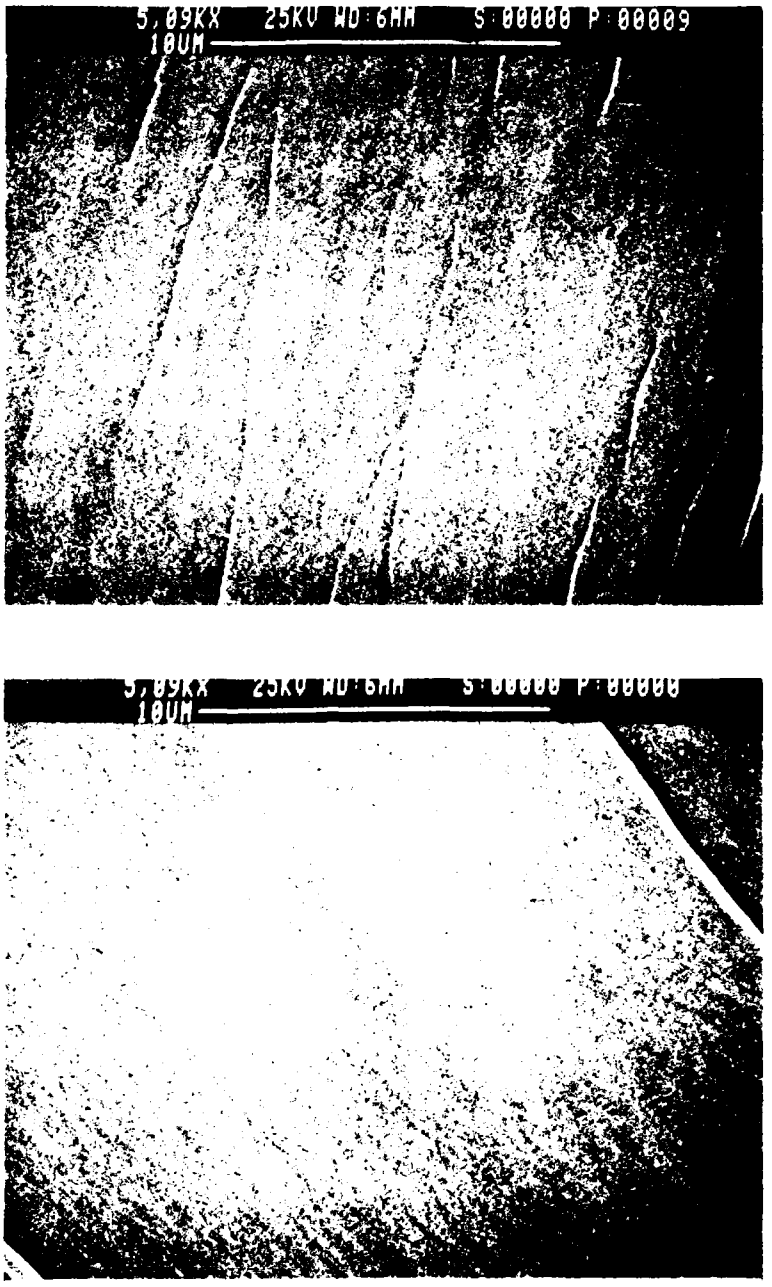


FIGURE 2.20
FRACTURE SURFACE OF m-ATB

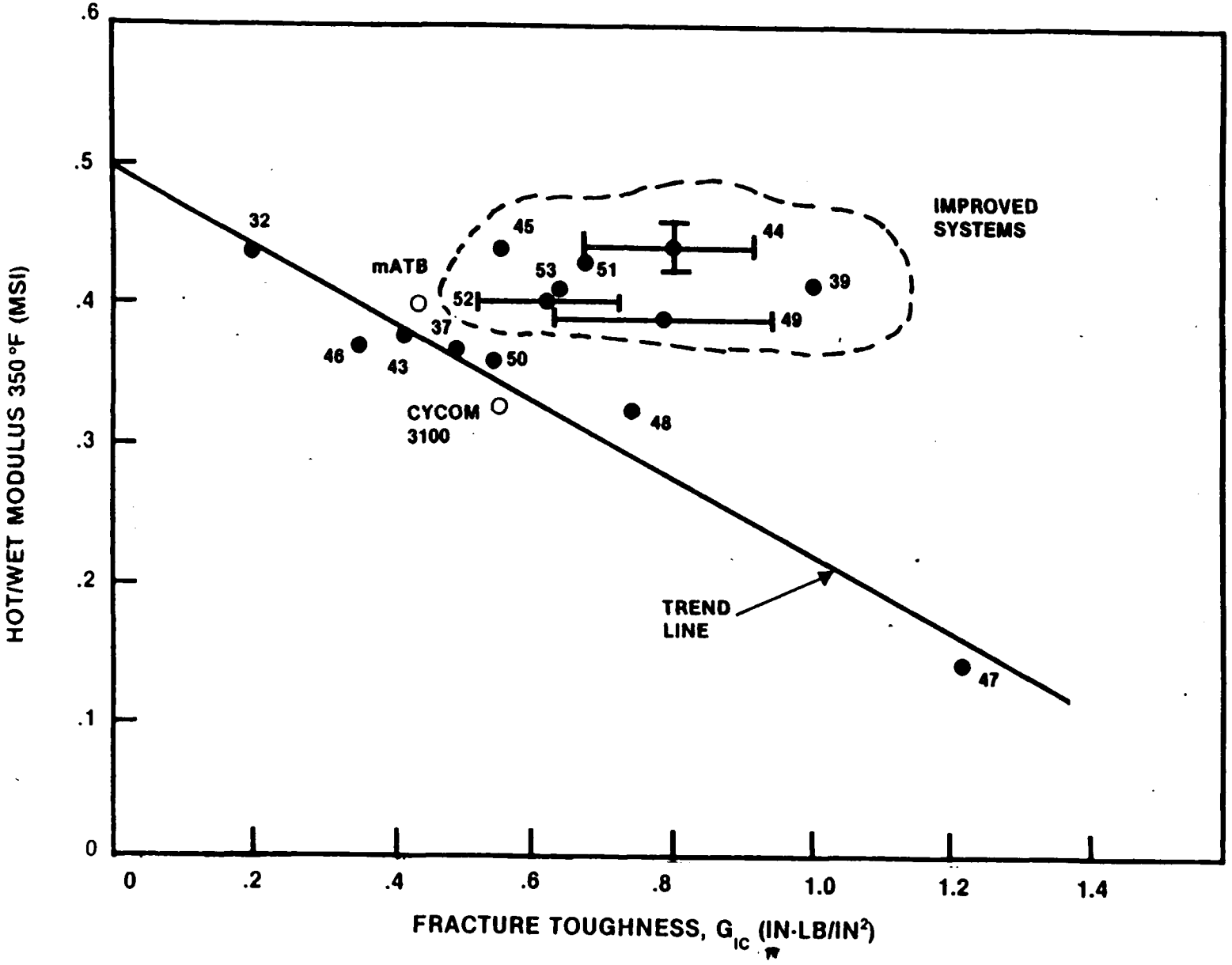


FIGURE 2.21 FRACTURE TOUGHNESS AND HOT/WET MODULUS OF CATB FORMULATIONS

upper right quadrant of the plot. These resins have the best trade off between hot/wet and toughness properties. CATB-39, which is also in the high toughness regime, is made in such a way that it is not practical to make into prepreg with normal processing methods.

To clarify the use temperature in these formulations, the wet modulus as a function of temperature is shown in Figure 2.22. To maintain a hot/wet modulus at 232°C, only CATB-32 is satisfactory. For 204°C (400°F) service, CATB-44 has a sufficiently high modulus. For 177°C (350°F) service CATB-51 and CATB-49 are also suitable.

The moisture absorption of the selected ATB formulations is shown in Figure 2.23. For comparison, m-ATB and a bismaleimide, CYCOM 3100 and an spoxy CYCOM 985 are included. Though the moisture absorption of the formulated systems is significantly higher than m-ATB, they still have a far lower moisture absorption than BMI's or epoxies.

In conclusion, CATB-44 and -51 were recommended and approved for scale-up into prepreg tape because these systems showed a good balance of properties (for applications up to 400-425°F) and processability characteristics. All three systems selected show higher fracture toughness than m-ATB or the state-of-the-art bismaleimide system CYCOM 3100. CATB-32 was an alternative system for 450°F/wet performance, but it was thought that the brittleness of this system would lead to microcracking.

Thus, it was recommended and approved that CATB-44 and -51 be scaled up and evaluated in a composite for 400-425°F applications and CATB-49 for 350°F applications.

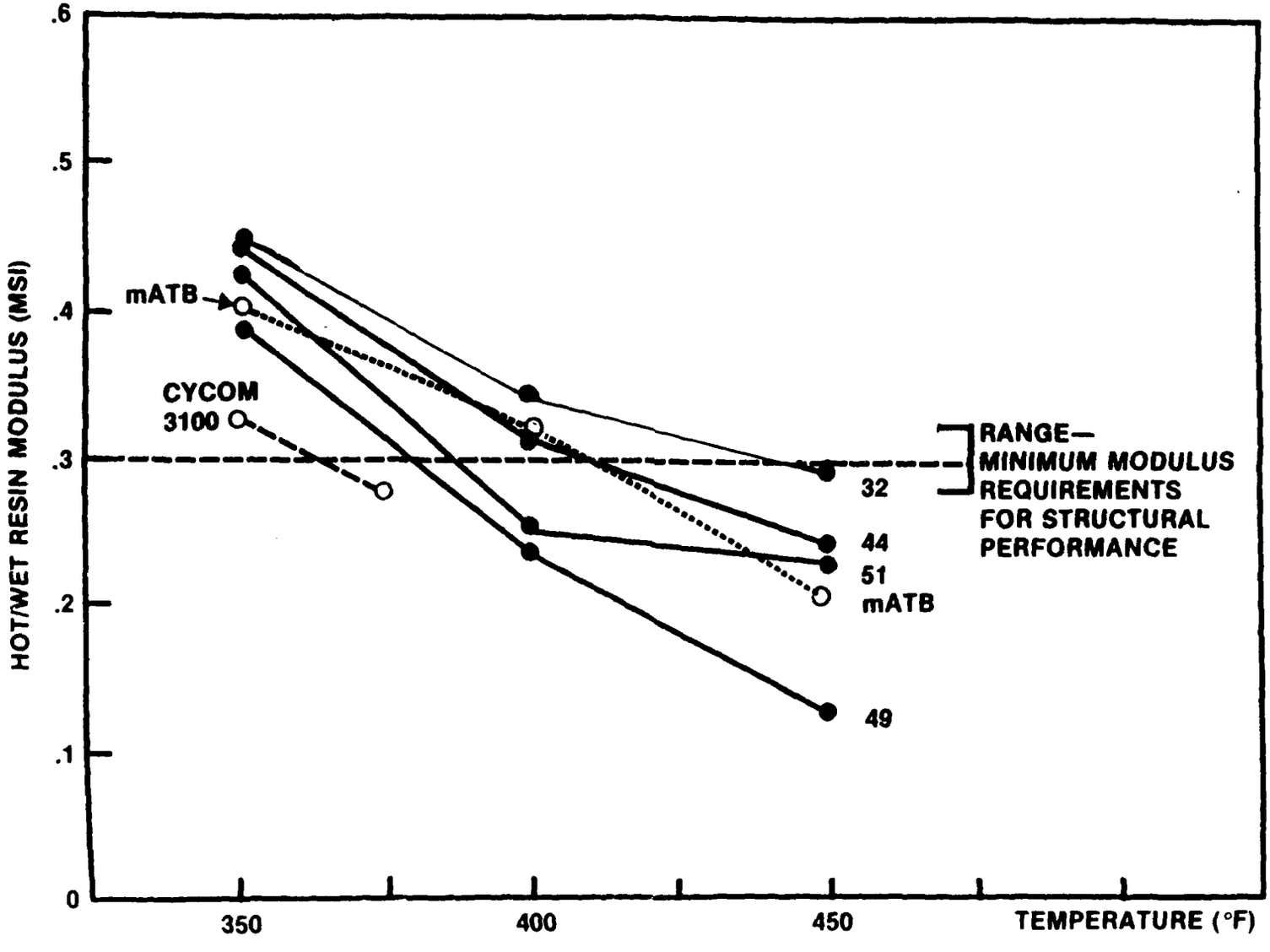


FIGURE 2.22

COMPARISON OF HOT/WET MODULUS
vs
TEMPERTURE FOR CATB FORMULATIONS

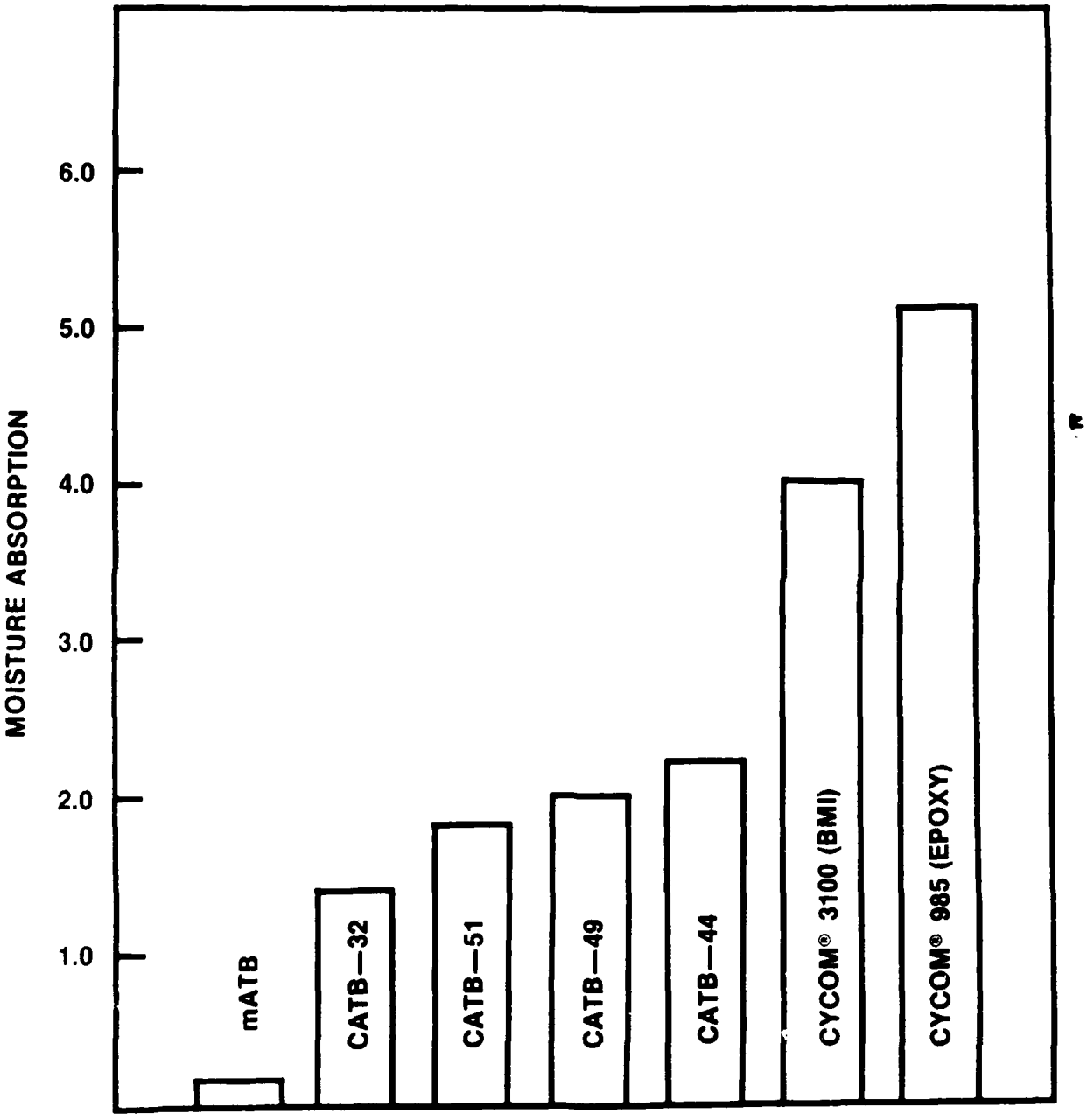


FIGURE 2.23

MOISTURE ABSORPTION OF CATB FORMULATIONS

2.3 m-ATS FORMULATION

2.3.1 Preliminary Screening

m-ATS Substitution in m-ATB Formulations

To compare m-ATS and m-ATB in formulated systems, three optimal m-ATB formulations were mixed, directly substituting m-ATS for m-ATB. Rheological, mechanical, and thermal properties were measured and compared to the properties of the corresponding m-ATB formulation, as shown in Tables 2.13, 2.14 and 2.15. m-ATS formulations had about double the viscosity at 71°C and about 4 times the minimum viscosity of corresponding m-ATB formulations. Minimum viscosities occurred at around 160°C compared to 130°C for m-ATB formulations. m-ATS caused an increase in glass transition temperature, Tg, and dry modulus, E_D, and an increase in water absorption. Hot/wet moduli and toughness, G_{IC}, of CATB-44 were not changed when m-ATS was substituted for m-ATB. However, in CATB-49 and -51 formulations, m-ATS improved hot/wet moduli and decreased toughness.

Alternate m-ATS Formulations

Twenty-four formulations were evaluated in the preliminary screen. The results are listed in Table 2.16. The formulations were evaluated to determine compatibility, tack, and out-time. Formulations were sought that would increase tack and toughness. ATS was more compatible with reactive and non-reactive modifiers than m-ATB resins. ATS is a solid at room temperature, which reduces or eliminates tack of formulated resins. Tackifiers were used to increase tack. However, when it was raised to acceptable levels, mechanical properties suffered. This contrasts with m-ATB formulations, a number of which have good tack.

TABLE 2.13

m-ATS FORMULATION DEVELOPMENT-NEAT RESIN FLEXURAL PROPERTIES

Formulation	Tg°C			Modulus 23°C, Dry (MSI)	Strength 23°C, Dry (KSI)	Strain to Failure (%)	Work to Break in-lb/in^3	Water Absorption %	G_{IC} (in-lb/in^2)
	Tan Delta	Modulus Intercept	5% Offset						
CATS-1 (m-ATB in CATB-44 replaced with m-ATS)	303	274	268	0.622 ±0.012	19.1 ±0.6	3.1 ±0.1	300 ±20	3.0	0.66
CATB-44	286	265	253	0.579 ±0.003	17.4 ±2.6	2.8 ±.07	298 ±100	2.58	0.63
CATS-2 (m-ATB in CATB-49 replaced with m-ATS)	287	256	246	0.617 ±0.007	19.7 ±1.2	3.2 ±0.2	320 ±40	2.59	0.67
CATB-49	274	246	215	0.601 ±0.008	21.1 ±2.3	3.5 ±0.4	392 ±88	1.99	0.7
CATS-3 (m-ATB in CATB-51 replaced with m-ATS	326	280	270	0.647 ±0.010	17.7 ±3.8	3.0 ±0.5	310 ±100	3.01	0.45
CATB-51	296	272	254	0.612 ±0.021	19.5 ±5.3	3.3 ±1.0	350 ±215	2.55	0.67

TABLE 2.14

HEAT RESIN EVALUATION - m-ATS FORMULATIONS
350°F (177°C)/WET

Formulation	Test Condition	Modulus (MSI)	Strength (KSI)	Strain To Failure %	Work to Break in-lb/In^3
CATS-1 (m-ATB in CATB-44 replaced with m-ATS)	177°C/wet	0.416 ±0.024	8.7 ±1.4	2.1 ±0.4	100 ±30
CATB-44	177°C/wet	0.418 ±0.009	11.7 ±0.8	2.8 ±0.3	170 ±30
CATS-2 (m-ATB in CATB-49 replaced with m-ATS)	177°C/wet	0.392 ±0.005	11.4 ±1.1	3.1 ±0.3	185 ±40
CATB-49	177°C/wet	0.388 ±0.010	12.4 ±1.3	3.7 ±0.4	240 ±65
CATS-3 (m-ATB in CATB-51 replaced with m-ATS)	177°C/wet	0.424 ±0.039	8.2 ±1.2	1.9 ±0.2	80 ±20
CATB-51	177°C/wet	0.427 ±0.021	10.3 ±3.2	2.5 ±0.7	135 ±85

TABLE 2.15
NEAT RESIN EVALUATION - m-ATS FORMULATIONS
450°F (232°C)/WET

Formulation I.D.	Test Condition	Modulus (MSI)	Strength (KSI)	Strain %
CATS-1 (m-ATB in CATB-44 replaced with m-ATS)	232°C/wet	0.237 ±0.021	5.1 ±0.7	2.3 ±0.1
CATB-44	232°C/wet	0.245 ±0.016	7.1 ±0.6	3.2 ±0.6
CATS-2 (m-ATB in CATB-49 replaced with m-ATS)	232°C/wet	0.199 ±0.003	5.8 ±0.7	8.8 ±0.6
CATB-49	232°C/wet	0.127 ±0.021	4.8 ±0.3	5.9 ±2.2
CATS-3 (m-ATB in CATB-51 replaced with m-ATS)	232°C/wet	0.261 ±0.010	6.9 ±1.2	2.9 ±0.6
CATB-51	232°C/wet	0.237 ±0.015	6.9 ±0.1	3.1 ±0.1

TABLE 2.16

[redacted]

Formulation #	Notebook #	DMA, Tg°C Tan Delta	DMA, Tg°C Mod. Int.	DMA, Tg°C 5% Offset	RT Flex Properties Modulus (MSI)	RT Flex Properties Strength (KSI)	RT Flex Properties Strain (%)	Comments
CATS-4	S15401-167-2	348	290	279	0.630	12.5	2.0	Clear homogeneous casti no voids.
CATS-5	S15401-172-1	-	-	-	-	-	-	Incompatiable mixture, could not be cast.
CATS-6	S15401-172-2	-	-	-	-	-	-	Inhomogeneous casting, not tested.
CATS-7	S15401-172-3	-	-	-	-	-	-	Casting full of voids, not tested.
CATS-8	S15401-168-1	-	-	-	-	-	-	Too viscous to cast.
CATS-9	S15401-168-2	-	-	-	-	-	-	Casting was full of voids not tested.
CATS-10	S15597-4-1	281	261	259	0.557	11.5	2.1	Dark brown casting, no voids, no tack at RT.
CATS-11	S15597-4-2	304	238	233	-	-	-	Casting had voids, not tested under flex.
CATS-12	S15597-5-2	-	-	-	-	-	-	Casting was full of voids not tested.
CATS-13	S15597-5-3	340	275	272	0.574	12.9	2.3	Dark brown casting, no voids, no tack at RT.
CATS-14	S15597-5-4	305	260	250	-	-	-	Casting had surface problems, not tested under flex, no tack at RT.
CATS-15	S15597-18-1	303	279	272	0.612	16.1	2.5	Dark brown coating no voids, no tack at RT.
CATS-16	S15597-18-2	304	274	260	0.602	15.3	2.6	Dark brown casting, no voids, no tack at RT.
CATS-17	S15597-18-3	291	272	271	0.633	13.9	2.2	Dark brown casting, no voids, no tack at RT.
CATS-18	S15597-32-1	-	-	-	0.593	14.2	2.6	Inhomogeneous casting.
CATS-19	S15597-32-2	-	-	-	-	-	-	Too viscous to cast.
CATS-20	S15671-23-1	-	-	-	-	-	-	Too viscous to cast
CATS-21	S15671-23-2	-	-	-	-	-	-	Large voids
CATS-22	S15671-23-3	-	-	-	.	-	-	Brittle, voidy casting
CATS-23	S15671-30-1	274	253	247	.593	8.6	1.5	Dark brown casting, no voids, No tack at RT
CATS-24	S15671-30-2	278	257	264	.609	11.9	2.0	Dark brown casting, no voids. No tack at RT

2.3.2 Comprehensive Screening

The ten m-ATS formulations selected for comprehensive resin screening included those that were successfully cast during the preliminary screen.

A summary of tests and test specimens used in the comprehensive resin screen is shown in Table 2.8. Target values are given in Table 2.6.

Results

The cure of m-ATS formulations and the mechanical, thermal and water absorbing properties of cured m-ATS formulations were measured.

DSC Characterization

DSC analyses of the cure of several formulations are given in Table 2.17. Generally, the maximum in the cure exotherm was around 260°C , well above that of m-ATS, which was around 230°C. The heat of polymerization of formulated systems was lower than that of m-ATS itself.

Flexural Stress-Strain and Dynamic Mechanical Analysis

The flexural properties of the ten m-ATS formulations are given in Table 2.18. Also included are the glass transition temperatures determined by dynamic mechanical analytsis (DMA). Tables 2.19 and 2.20 have hot/wet flexure data at 177°C (350°F) and 232°C (450°F) for several formulations. CATS-15, -16 and -17 have superior high temperature properties, with a modulus at 232°C/wet of about 0.3 MSI.

TABLE 2.17

DSC ANALYSIS OF m-ATS RESIN FORMULATIONS

CATS #	Exotherm Onset Temp. °C	Exotherm Peak Temp. °C	Exotherm Completion Temp. °C	Heat of Polymerization Cal/g
m-ATS	144	227	292	110
CATS-1	162	264	364	84
CATS-2	172	267	315	53
CATS-3	162	262	335	75
CATS-4	171	253	334	84

TABLE 2.18 COMPREHENSIVE NEAT RESIN SCREEN - m-ATS FORMULATIONS

Formulation	Tg°C Tan Delta	Tg°C Modulus Intercept	Tg°C 5% Offset	Modulus 23°C, Dry (MSI)	Strength 23°C, Dry (KSI)	Strain to Failure (%)	Work to Break in-lb/in^3	Water Absorption %
CATS-1	303	274	268	0.622 ±0.012	19.1 ±0.6	3.1 ±0.1	300 ±20	3.0
CATS-2	287	256	246	0.617 ±0.007	19.7 ±1.2	3.2 ±0.2	320 ±40	2.59
CATS-3	326	280	270	0.647 ±0.010	17.7 ±3.8	3.0 ±0.5	310 ±100	3.01
CATS-4	350			0.630 ±0.008	12.5 ±2.4	2.0 ±0.4	127 ±47	3.0
CATS-10	281	261	259	0.557 ±0.007	11.5 ±1.5	2.05 ±0.3	120 ±30	-
CATS-13	340	275	272	0.574 ±0.008	12.9 ±1.2	2.3 ±0.2	-	-
CATS-15	303	279	272	0.612 ±0.008	16.1 ±1.9	2.5	-	2.42
CATS-16	304	274	260	0.602 ±0.006	15.3 ±1.9	2.6 ±0.3	-	2.03
CATS-17	291	272	271	0.633 ±0.001	13.9 ±3.2	2.2 ±0.5	-	2.62
CATS-23	274	253	247	0.593 ±0.015	8.6 ±1.1	1.5 ±.2	66 ±17	-
CATS-24	278	257	264	0.609 ±.008	11.9 ±0.6	2.0 ±.1	119 ±11	-

TABLE 2.19

COMPREHENSIVE NEAT RESIN EVALUATION - m-ATS FORMULATIONS
350°F (177°C)/WET

Formulation	Test Condition	Modulus (MSI)	Strength (KSI)	Strain To Failure %	Work to Break in-lb/In^3
CATS-1	177°C/wet	0.416 ±0.024	8.7 ±1.4	2.1 ±0.4	100 ±30
CATS-2	177°C/wet	0.392 ±0.005	11.4 ±1.1	3.1 ±0.3	185 ±40
CATS-3	177°C/wet	0.424 ±0.039	8.2 ±1.2	1.9 ±0.2	80 ±20
CATS-15	177°C/Wet	0.452 ±0.022	7.0 ±2.4	1.7 ±0.5	-
CATS-16	177°C/Wet	0.435 ±0.006	7.3 ±2.4	1.8 ±0.6	-
CATS-17	177°C/Wet	0.456 ±0.010	5.8 ±1.3	1.4 ±0.3	-

TABLE 2.20

COMPREHENSIVE NEAT RESIN EVALUATION - m-ATS FORMULATIONS
450°F (232°C)/WET

Formulation I.D.	Test Condition	Modulus (MSI)	Strength (KSI)	Strain %
CATS-1	232°C/wet	0.237 ±0.021	5.1 ±0.7	2.3 ±0.1
CATS-2	232°C/wet	0.199 ±0.003	5.8 ±0.7	8.8 ±0.6
CATS-3	232°C/wet	0.261 ±0.010	6.9 ±1.2	2.9 ±0.6
CATS-15	232°C/Wet	0.314 ±0.018	5.1 ±1.3	1.7 ±0.5
CATS-16	232°C/Wet	0.297 ±0.009	5.1 ±1.6	1.8 ±0.6
CATS-17	232°C/Wet	0.316 ±0.2	4.8 ±0.6	1.6 ±0.1

Fracture Toughness

Fracture toughness, as measured using compact tension specimens, is given in Table 2.21. All formulations were tougher than m-ATS itself, which had a critical strain energy release rate, G_{IC}, of only 0.12 in-lb/in^2. Those with superior hot/wet flexural modulus, CATS-15, -16, and -17, had a G_{IC} of only 0.17 to 0.27 in-lb/in^2. The highest toughnesses obtained were in the range of 0.67 in-lb/in^2 for CATS-1 and -2.

Scanning Electron Microscopy

To evaluate the resin morphologies of m-ATS formulations, SEM analyses of the fracture surfaces of the failed compact tension specimens were examined. Similar to what was observed for m-ATB and m-ATB formulated systems, dramatic differences were seen in the m-ATS systems. The fracture surface of m-ATS was smooth and lacked significant fracture features. This is consistent with its low toughness. Comparison of fracture surfaces of the m-ATS formulated systems, CATS-1, -2 and -3 with those of analogous m-ATB systems shows that both m-ATS and m-ATB provide similar morphologies.

Effect of Post Cure Temperature

Early work on m-ATS resin found that a postcure temperature of 250°C gave properties equal to or better than those seen for resin postcured at 300°C. In order to confirm this for formulated resins, CATS-1, CATS-3 and CATS-15 were cast using both 250°C and 300°C postcures. Their fracture toughness and glass transition temperatures were then compared. The results are summarized in Table 2.22. They show that no significant increase in fracture toughness was seen at the higher postcure temperature.

TABLE 2.21

COMPREHENSIVE NEAT RESIN EVALUATIONS - m-ATS FORMULATIONS FRACTURE TOUGHNESS

SAMPLE	G_{IC} (IN-LB/IN^2)
m-ATS	0.12
m-ATS	0.43
CATS-1	0.66
CATB-44	0.67*
CATS-2	0.67
CATB-49	0.77*
CATS-3	0.45
CATB-51	0.64*
CATS-4	0.24
CATS-15	0.27
CATS-16	0.17
CATS-17	0.25
CATS-23	0.23
CATS-24	0.25
CYCOM 3100	0.55

*Average of Three Specimens

TABLE 2.22

m-ATS COMPACT TENSIONS VS. POST CURE TEMPERATURE

Material	Post Cure Temp°C	Energy in lbs/in^3	K1C
CATS-1 (15559-97-2)	250	0.46	0.589±0.012
	300	0.32	0.514
Old CATS-1 (15597-14-1)	250	0.38	0.642±0.052
CATS-3 (15559-97-3)	250	0.28	0.480±0.027
	300	0.22	0.473±0.022
Old CATS-3 (15597-14-3)	250	0.27	0.540±0.066
CATS-15 (15559-97-4)	250	0.16	0.356
	300	0.16	0.314
Old CATS-15 (15597-18-1)	250	0.14	0.409

2.3.3 Conclusions

The best three m-ATS systems which could be recommended for tape scale-up are CATS-1 for 177°C (350°C)/wet performance; CATS-3 for 204°C/(400°F)/wet performance; and CATS-15 for 450°F performance. However, the balance of toughness and elevated temperature performance of the m-ATS formulations lie within the range seen for the m-ATB formulations. This can be seen from the plot of 350°F/wet flexural modulus vs. G_{IC} for neat m-ATS and m-ATB resin shown in Figure 2.24, and in the plot showing 450°F/wet data (Figure 2.25).

Furthermore, for a given modulus at 177°C (350°F)/wet, the m-ATB formulations show greater fracture toughness. For these reasons, it was recommended and approved that subsequent work concentrate on m-ATB formulations with the goal of improving the matrix-fiber interface.

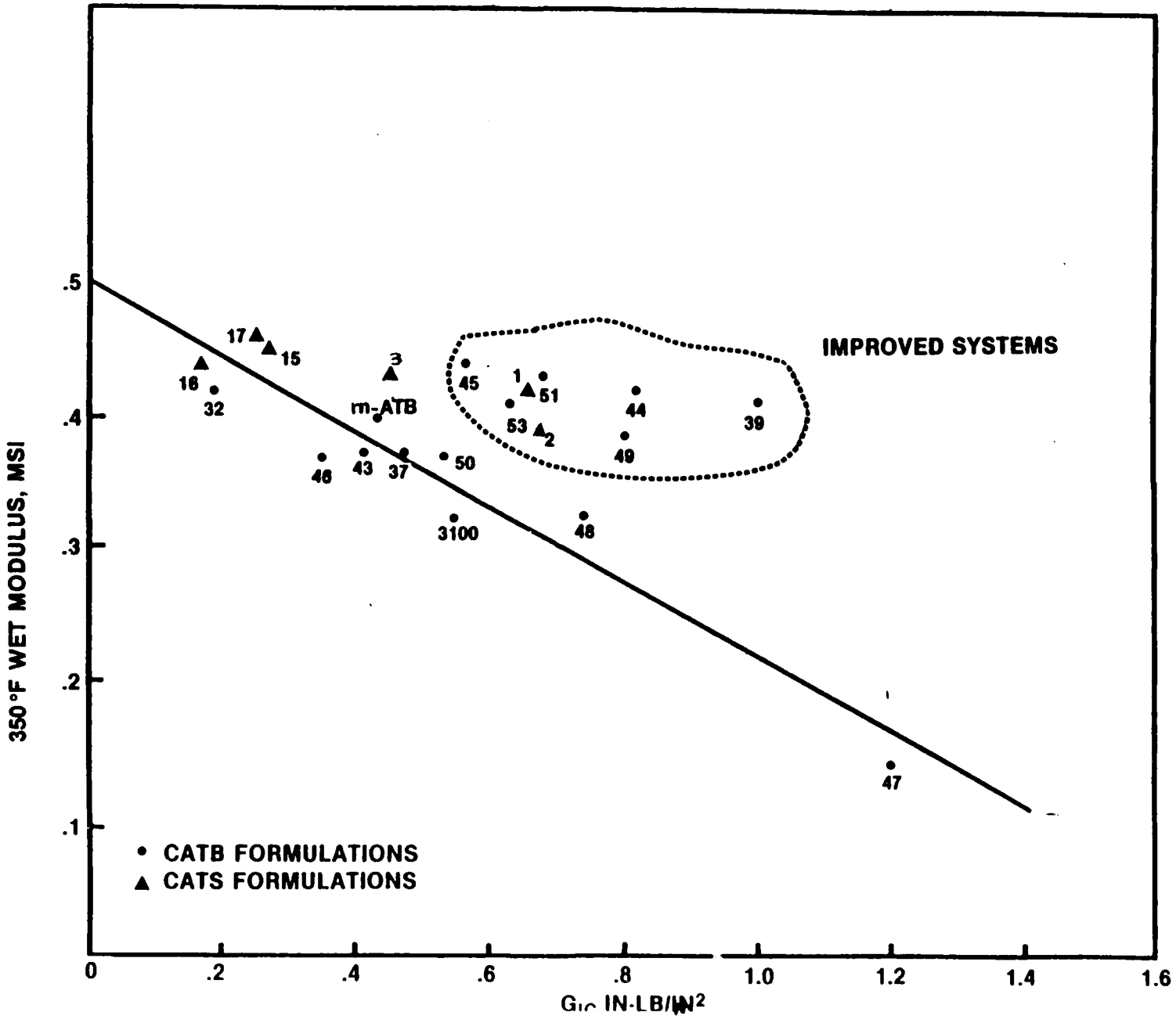


FIGURE 2.24 FRACTURE TOUGHNESS AND 350°F HOT/WET MODULUS OF AT RESIN FORMULATIONS

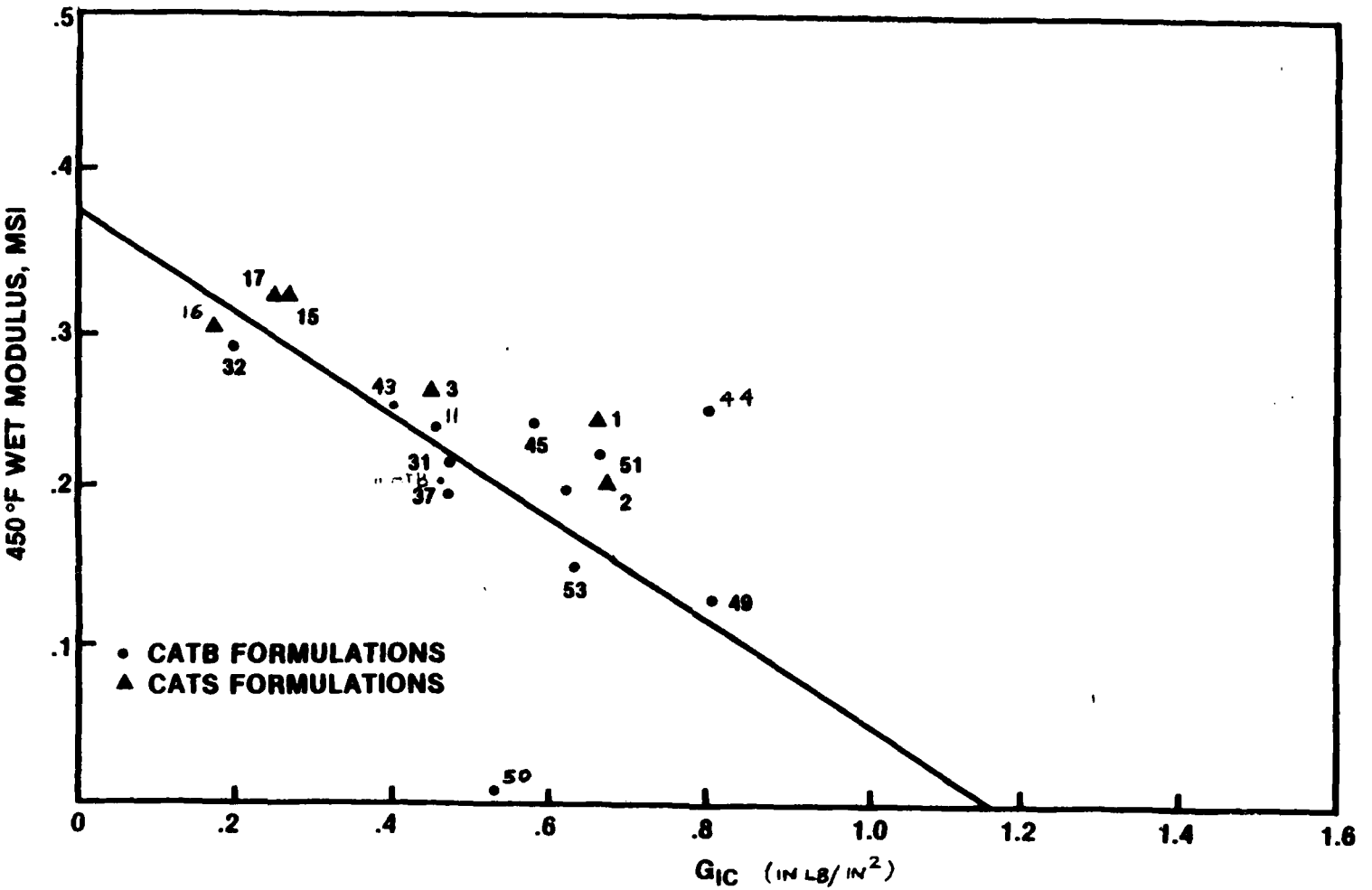


FIGURE 2.25
FRACTURE TOUGHNESS AND 450°F HOT/WET MODULUS OF AT RESIN FORMULATIONS

3.0 TASK II: PRELIMINARY PREPREG EVALUATION

In Task II, the effect of fiber sizing and the effect of particular selecting either AS-4 or T300 as the reinforcing fiber, was determined. Three m-ATB formulations were selected and scaled-up to prepreg on a commercial production tape machine. The prepreg was characterized and an optimal cure cycle was determined.

3.1 FIBER - RESIN ADHESION

Unsized and "G-sized" AS-4 and unsized T300 carbon fibers were compared using CATB-32 and -44 resin formulations.

3.1.1 Effect of Sizing on AS-4/CATB-32 and -44

Two formulations, CATB-32 and CATB-44, were made into 0.075" thick unidirectional tape laminates using both unsized and "G-sized" AS-4 fiber to assess the quality of the bond between the resins and the fiber.

12K tows were wrapped around a 12-inch long elliptical mandrel. This simulated a winding drum with a radius of 2 feet. The tows were spaced at 10 tows per inch across 6 inches. The resin, in the form of a 28% solids solution in methylene chloride (MeCl), was worked into the tows with a putty knife to achieve a 38% resin content. The solvent was driven off, and 3 inch x 6 inch (0°) plies were cut and stacked eight plies thick.

The laminates were bagged without bleeders. The cure cycle was as follows:

a) Precompaction at room temperature under vacuum and 100 psi pressure for 30 minutes
b) Vent vacuum and raise to 150°C under 100 psi pressure at 3-5°C per minute

c) Hold at 150°C for 90 minutes
d) Raise to 177°C at 3°C per minute
e) Hold at 177°C for 4 hours
f) Cool to RT at 3°C per minute
g) Postcure 4 hrs at 250°C in circulating air oven

Short beam shear specimens were prepared and tested according to ASTM D2344 [73]. The test was selected due to the limited amount of material. The results are given in Table 3.1. The dry short beam shear test results indicated little difference between the two sizes. After hot/wet conditioning, elevated temperature SBSS indicated that unsized AS-4 fiber showed a small advantage over "G-sized" AS-4. Thus, use of unsized fiber was recommended and approved for future scale-up.

The fracture surface of these scaled-up systems were examined using scanning electron microscopy to determine the effect of sizing on fiber bonding. Specimens were 8 ply, unidirectional laminates and were failed in four point interlaminar shear. The samples examined were: CATB-32/unsized, CATB-32/"G-sized," CATB-44/unsized and CATB-44/"G-sized." All specimens showed evidence of adhesion of the matrix to the fiber. However, because the resin systems were relatively brittle, it was difficult to assess differences in bonding from such fracture surfaces. Little difference was seen between "G-sized" and unsized fibers. No ductility of matrix resin CATB-32 was evident, while limited plasticity was seen in matrix CATB-44.

3.1.2 Fiber-Resin Interface Study: Bonding to T300 Fiber

At the request of AFWAL, the fiber-matrix interface study was expanded to include unsized T300 fiber. As in the initial study, formulations CATB-32 and CATB-44 were made into 0.075" thick unidirectional laminates to assess the bond quality between the matrices and T300 fiber. The laminates were prepared and cured following the procedures just described.

TABLE 3.1

ATB LAMINATE FIBER EVALUATIONS (1)

SBBS, KSI

TEST CONDITION	CATB-32/ AS4 UNSIZED	CATB-32/ AS4 "G" SIZED	CATB-32/ T-300	CATB-44 AS4 UNSIZED	CATB-44/ AS4 "G" SIZED	CATB-44/ T-300
73°F Dry	13.8 ± .6	14.5 ± .5	12.9 ± 1.8	16.3 ± .6	15.3 ± .7	15.5 ± .2
450°F Dry	9.2 ± .1	9.4 ± .3	8.4 ± .2	9.3 ± .2	9.0 ± .1	7.5 ± .2
300°F Wet (A)	7.6 ± .3	7.7 ± .1	7.5 ± .5	8.3 ± .1	7.5 ± .1	6.8 ± .2
350°F Wet (A)	7.0 ± .2	6.7 + .2	6.5 ± .2	6.9 ± .1	6.2 ± .1	6.3 ± .2
400°F Wet (A)	5.5 ± .2	5.3 ± .1	5.8 ± .2	5.2 ± .1	4.6 ± .1	4.8 ± .2

(1) Laboratory prepared "Drum Wound" prepreg
(A) = 7 days H_2O @ 71°C

Short beam shear specimens were prepared and tested according to ASTM D2344 (1), and their properties were compared to the previously evaluated laminates which used unsized AS-4 and "G-sized" AS-4 fiber reinforcement. The results are also reported in Table 3.1. No significant difference in properties over unsized AS-4 fiber is noted when unsized T300 fiber is used as the reinforcement. Microscopic examination showed good adhesion to the T300 fiber.

3.2 PREPREG SCALE-UP

From the m-ATB formulations evaluated in the comprehensive neat resin screen, three formulations were selected for scale-up into prepreg. The three systems selected possessed a good combination of toughness, 177°C-232°C (350-450°F)/wet physical properties and processing characteristics. Nominal five-pound quantities of 12-inch wide prepreg were prepared from three formulations, CATB-44, CATB-49 and CATB-51, on unsized Hercules AS-4, 12K graphite fiber on a production tape machine at Cyanamid's Saugus, CA plant. The prepregs were evaluated initially for resin content, fiber areal weight, flow, volatiles, gel time, out-time and tack. Quality control data are summarized in Table 3.2. Test procedures are summarized in Appendix B.

3.3 PREPREG CHARACTERIZATION

3.3.1 Differential Scanning Calorimetry

The three scaled-up prepregs were analyzed using DSC and compared to the DSC curves of the neat resin. The curves are somewhat different from those of the neat resin in that the first exothermic peak seen in the neat resin is absent from the prepreg. In its place is an endothermic peak. The reason for this difference is that when resins are prepared for casting into plaques, they are mixed at higher temperatures than when being prepared for prepregging. In the latter case, a crystalline component is not

TABLE 3.2

QUALITY CONTROL DATA FOR PREPREG SCALE-UP

Formulation ID	Resin Content Weight %	FAW g/m^2	Flow	Volatiles %	Gel (Seconds) at 350°F	Out Time @ 75°F
CATB-44	32.7	147	13.6	0.49	609	> 7 day
CATB-49	33.1	145	11.1	1.2	625	> 7 day
CATB-51	32.8	146	16.3	0.76	654	> 7 day

dissolved completely. When this latter resin is heated in the DSC it shows a complex curve in which melting, dissolution, and reaction of the crystalline component occur in quick succession.

3.3.2 Short Beam Shear Strength

As a precursor to the comprehensive laminate evaluations, 16 ply unidirectional laminates, 3 x 3 inches, were prepared from each of the three scaled-up prepregs.

The laminates were bagged without bleeders using the bagging sequence shown in Figure 3.1. Cure cycle development work for the neat resins, described in Section 2.1.1 served as the basis for the cure cycle development for the modified m-ATB/AS-4 prepregs. The cure cycle was as follows:

a) Precompaction at room temperature under vacuum and 100 psi pressure for 30 minutes
b) Vent vacuum and raise to 150°C under 100 psi pressure at 3-5°C per minute
c) Hold at 150°C for 90 minutes
d) Raise to 177°C at 3°C per minute
e) Hold at 177°C for 4 hours
f) Cool to RT at 3°C per minute

A postcure cycle of 4 hours at 250°C followed.

This cure cycle resulted in high quality void-free laminates as determined from photomicroscopic examination of the polished edges of the cured laminates.

Short beam shear specimens were prepared and tested according to ASTM D2344 [73] because of the limited amount of material. The results are given in Table 3.3. At the elevated test temperature conditions, CATB-44 and CATB-51 showed similar short beam shear strengths while CATB-49 was slightly lower.

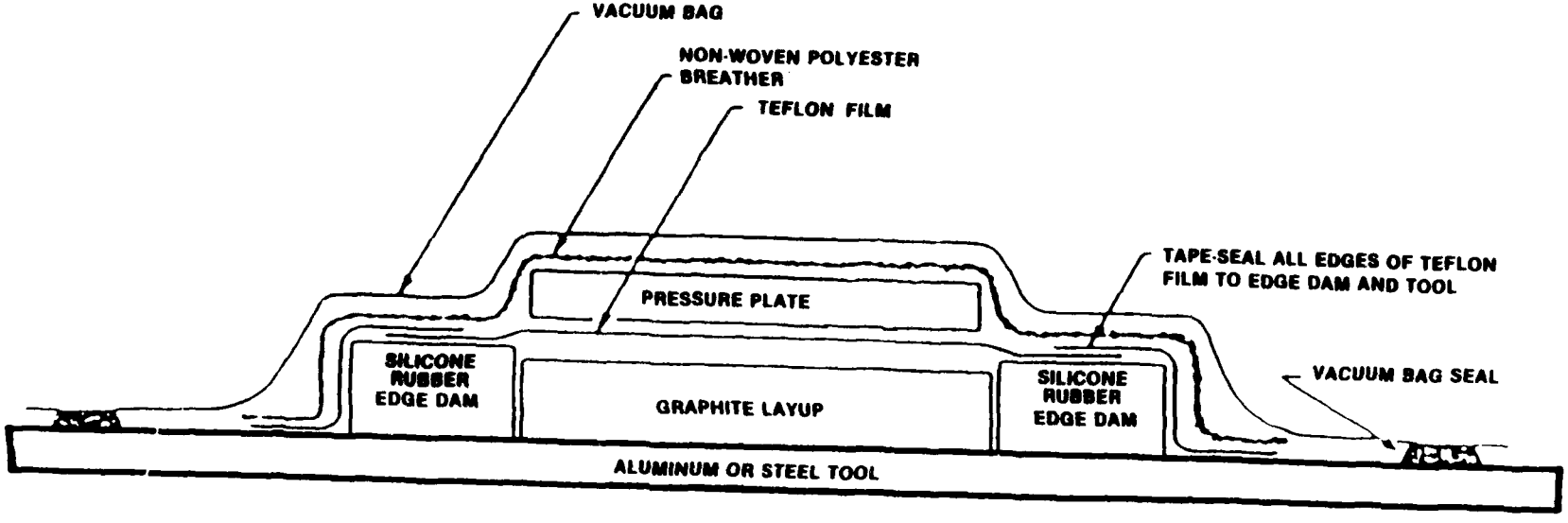


FIGURE 3.1

AT LAMINATE **BAGGING PROCEDURE**

TABLE 3.3

INITIAL CHARACTERIZATION OF ATB LAMINATES (1)

TEST CONDITION	SBSS, KSI CATB 44 82-51-24 AS4	 CATB 49 82-51-25 AS4	 CATB 51 82-51-23 AS4
23°C (73°F) Dry	16.9 ± .5	16.5 ± .4	17.3 ± .6
232°C (450°F) Dry	9.0 ± .1	7.4 ± .2	8.8 ± .2
177°C (350°F) Wet	7.5 ± .1	7.0 ± .1	7.1 ± .4
204°C (400°F) Wet	6.8 ± .1	5.8 ± .3	6.9 ± .1
232°C (450°F) Wet	5.8 ± .3	4.8 ± .2	4.9 ± .5

(1) Prepreg prepared on production type machine

3.4 CURE CYCLE DEVELOPMENT

Before curing the prepregs by the cure schedule that had been used in the resin formulation development, variations in cure cycle were investigated to determine whether or not they would result in different and better properties in the three formulations. It was possible that alterations in the network morphology might occur if different cure cycles were used. In particular, if a hold were made at a moderate temperature during cure it might allow a chain extension reaction to occur in preference to a crosslinking reaction.

Two features of the cure schedule were examined: the effect of an intermediate temperature hold at 150°C (302°F), and the effect of postcuring at a variety of temperatures.

3.4.1 Intermediate Temperature Hold

The effect of a 150°C (302°F) intermediate temperature hold was investigated. At 150°C the reaction was too slow to study by doing isothermal experiments in the DSC. Therefore, samples of CATB-44 were held at 150°C for various lengths of time from 1 minute to 19 hours. They were then heated in the DSC at 20°C/min to determine the resin's Tg and the amount of residual cure heat. The DSC traces for these resin specimens are shown in Figure 3.2. The effect of the 150°C hold on the resin's Tg and residual heat is summarized in Figure 3.3. At 150°C the cure takes about 12 to 15 hours to reach its maximum cure at that temperature. At that time, the resin's Tg is around 176°C.

From these results, it was decided to investigate the effect of such a hold on the resin's physical and dynamic mechanical properties by using two different hold times at 150°C during the cure cycle. Two resin castings each were made from CATB-44, -49 and -51. One casting of each formulation was then cured with a cure cycle that had a 1.5 hour hold at 150°C and the other casting

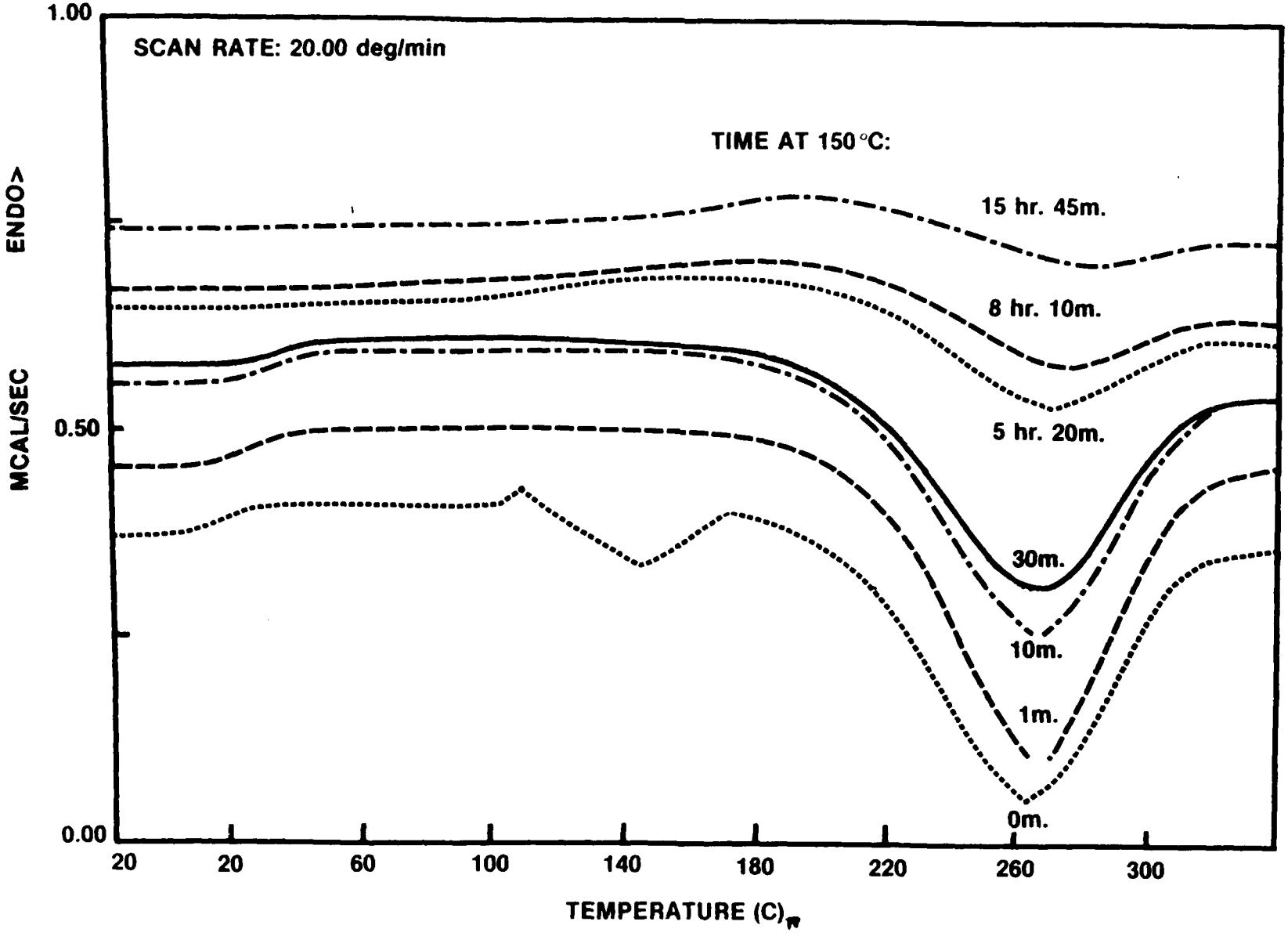


FIGURE 3.2 DSC OF CURED PREPREG RESIN

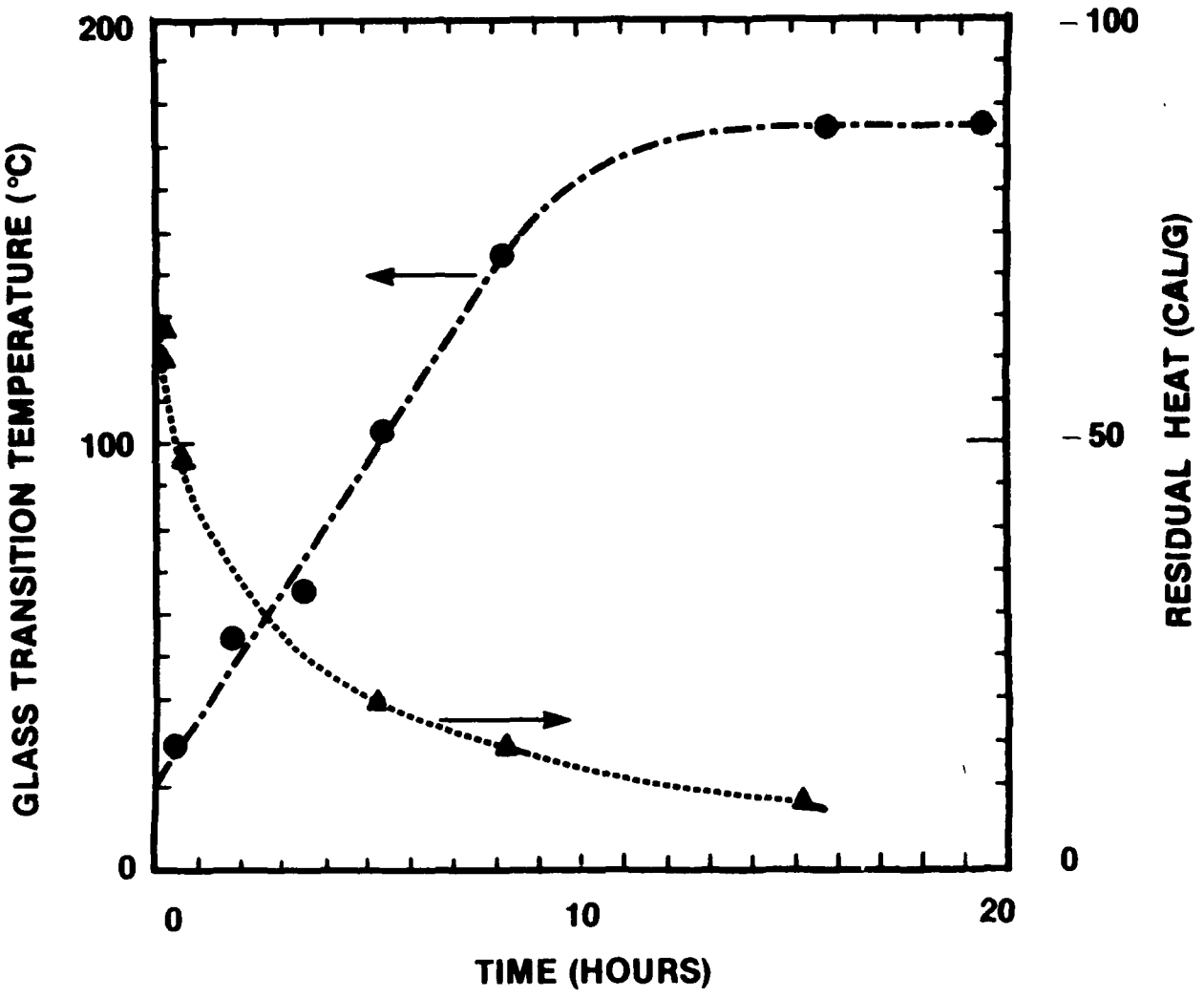


FIGURE 3.3
EFFECT OF 150°C ISOTHERMAL HOLD
ON CATB-44 RESIN NETWORK STRUCTURE

of each formulation was cured with a cycle that had a 15 hour hold at 150°C. During the remainder of the cure and postcure cycles, the two sets of castings were cured together using a four hour cure at 177°C and a four hour postcure at 250°C. Fracture toughness, flexural properties and Dynamic Mechanical Analysis were carried out to determine if this very different cycle had an effect on the mechanical properties at room temperature. The toughness properties were of particular interest. The results of these tests are shown in Table 3.4.

The thermal and mechanical properties were not found to vary significantly with cure cycle, though strain to failure appeared to be slightly higher for the long hold at 150°C. However, this difference was not significant enough to justify a change in cure cycle. Therefore, a 1.5 hour hold at 150°C was selected for the laminate cure cycle.

3.4.2 Postcure

Three postcure conditions were evaluated for their effects on laminate microcracking and Tg. The conditions chosen were 4 hours at 230°C (i.e., the CYCOM 3100 BMI postcure), 4 hours at 250°C (i.e., the standard ATB postcure), and 4 hours at 300°C. The latter condition was chosen because it was shown by Dynes [74] to significantly raise the Tg of unmodified ATB resin, but at the expense of severely degrading the resin's mechanical properties.

Six inch by six inch, 8 ply laminates were prepared from prepregs CATB-44, -49 and -51. The initial laminate stacking sequence was $(0, \pm 45, 0)_s$. This is the sequence used initially by McKague [75] in studies of bismaleimide laminate microcracking at General Dynamics in their evaluation of high temperature performance systems which included V378A.

TABLE 3.4

EFFECT OF INTERMEDIATE TEMPERATURE HOLD ON NEAT RESIN PROPERTIES FOR m-ATB FORMULATIONS

Formulation	Hold Time at 150°C (hr)	Tg, °C	Flexural Properties: Modulus GPa	Modulus (MSI)	Strength MPa	Strength (KSI)	Strain %	Work-to-Break MJ/m^3	Work-to-Break $(in\text{-}lbs/in^3)$	Fracture Toughness G_{IC} J/m^2	Fracture Toughness $(in\text{-}lb)/in^2$
CATB-44	1.5	302	4.16 ±.23	(.603 ±.034)	103 ±23	(14.9 ±3.4)	2.4 ±.6	1.3 ±.6	189 ±89	145. ±2.	(0.83 ±.01)
	15.	298	4.1 ±.03	(.599 ±.005)	152 ±23	(22.1 ±3.4)	3.3 ±.6	3.1 ±.9	456 ±138	162. ±17.	(0.94 ±.10)
CATB-49	1.5	285	4.24 ±.06	(.615 ±.008)	123 ±10	(17.9 ±1.4)	2.9 ±.3	1.8 ±.3	266 ±47	126. ±17.	(0.73 ±.10)
	15.	286	4.25 ±0.12	(.616 ±.017)	143 ±16	(20.8 ±2.3)	3.5 ±.4	2.6 ±.6	382 ±90	129. ±10.	(0.75 ±.06)
CATB-51	1.5	299	4.26 ±0.05	(.617 ±.007)	111 ±17	(16.1 ±2.4)	2.6 ±.4	1.5 ±.4	217 ±60	114. ±2.	(0.66 ±.01)
	15.	297	4.19 ±.09	(.607 ±.013)	137 ±14	(19.8 ±2.0)	3.3 ±.4	2.3 ±.5	337 ±77	117. ±19.	(0.68 ±.11)

The laminates were bagged without bleeders, as shown in Figure 3.1, and cured using the schedule described in Section 3.3.2 of this report. The laminates were cut into 3" x 3" squares, with one piece from each formulation postcured at either 230°C, 250°C, or 300°C.

Glass Transition Temperature

Dry Tg's by DMA were determined on the nine postcured panels. The results are summarized in Table 3.5.

Two attributes of the Dynamic Mechanical profiles are reported as a measure of Tg: the peak in the loss tangent curve (Tan delta), which corresponds to the values reported in the neat resin screen; and the modulus intercept, which is the intersection of tangent lines drawn along the pre-Tg and declining portion of the modulus curve. The modulus intercept more closely represents upper use temperature of the composite system.

A slight increase in Tg was produced by a 250°C postcure compared to the 230°C postcure. The 300°C postcure did not raise Tg significantly, and in the case of CATB-49 lowered Tg, perhaps due to matrix degradation. The three systems ranked in order of descending Tg: CATB-44, CATB-51 and CATB-49. All three systems had dry Tg's higher than unmodified ATB.

Microcracking

Polished cross-sections of the nine postcured panels were examined by SEM. Thorough examination uncovered no microcracking in any laminate.

Because no microcracking was produced in this laminate stacking sequence by any of the three postcures, three additional laminates were made using a stacking sequence of $(0,90_2,0)_s$, which produces more severe residual stress in the cured laminate.

TABLE 3.5

EFFECT OF POSTCURE TEMPERATURE ON GLASS TRANSITION OF ATB LAMINATES

Postcure	Glass Transition	Tg, °C CATB-44/AS-4	CATB-49/AS-4	CATB-51/AS-4
4 hr @ 230°C	Tan Delta	302	281	300
	Mod. Int.	253	238	248
4 hr @ 250°C	Tan Delta	299	287	303
	Mod. Int.	265	253	263
4 hr @ 300°C	Tan Delta	305	264	294
	Mod. Int.	278	218	255

NOTE: 8 Ply Laminates $[0/\pm 45/0]_s$

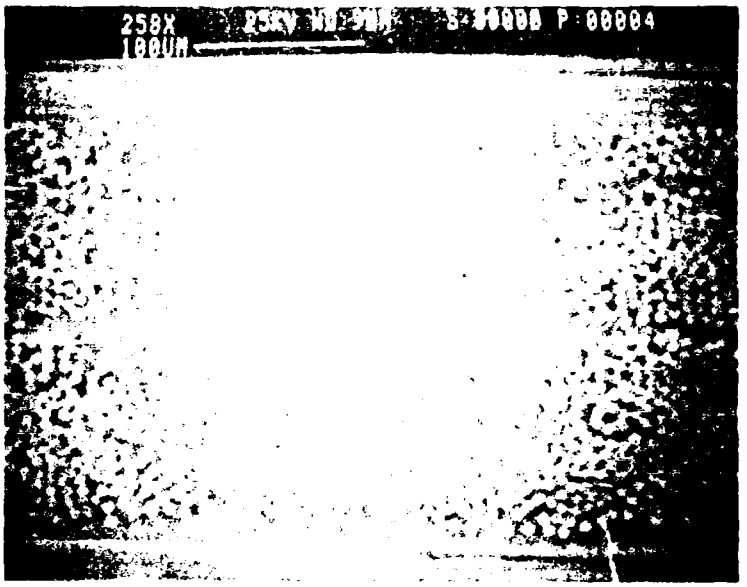
Typical Tg of CYCOM 3100 BMI Tan Delta 282°C - 315°C
Mod. Int. 235°C - 246°C

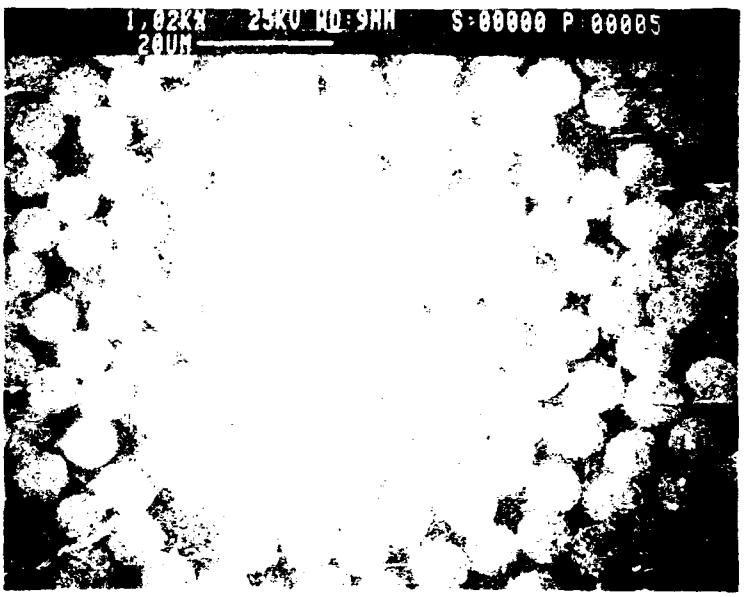
One piece from each panel was postcured 4 hours at 230°C and another piece was postcured 4 hours at 250°C. Photomicrographs of polished cross-sections again showed no microcracking for the panels that were postcured at 230°C. However, cracks had developed in all three laminates postcured at 250°C. These cracks were not the classical, periodic type associated with brittle resin microcracking, but appeared to be caused by matrix-fiber debonding. Photomicrographs showing these cracks are shown in Figures 3.4 through 3.6.

As a result of these studies, a postcure of 230°C was recommended and approved since it resulted in only a slight decrease in Tg from the 250°C postcured samples and prevented microcracking in laminates with high residual stresses. The Tg values of CATB-44, CATB-49, CATB-51 postcured at 230°C were within or exceeded the target range, i.e., a Tg of 204-260°C, measured by modulus intercept.

3.4.3 Conclusion

Based on this work, the bagging sequence shown in Figure 3.1 and the cure cycle shown in Figure 3.7 were selected for preparing laminates for comprehensive mechanical evaluations.





Photomicrographs of AS4/CATB-44 laminate, 0° view.

Postcure: 4 hr @ 250 °C, Layup $(0,90_2,0)_S$

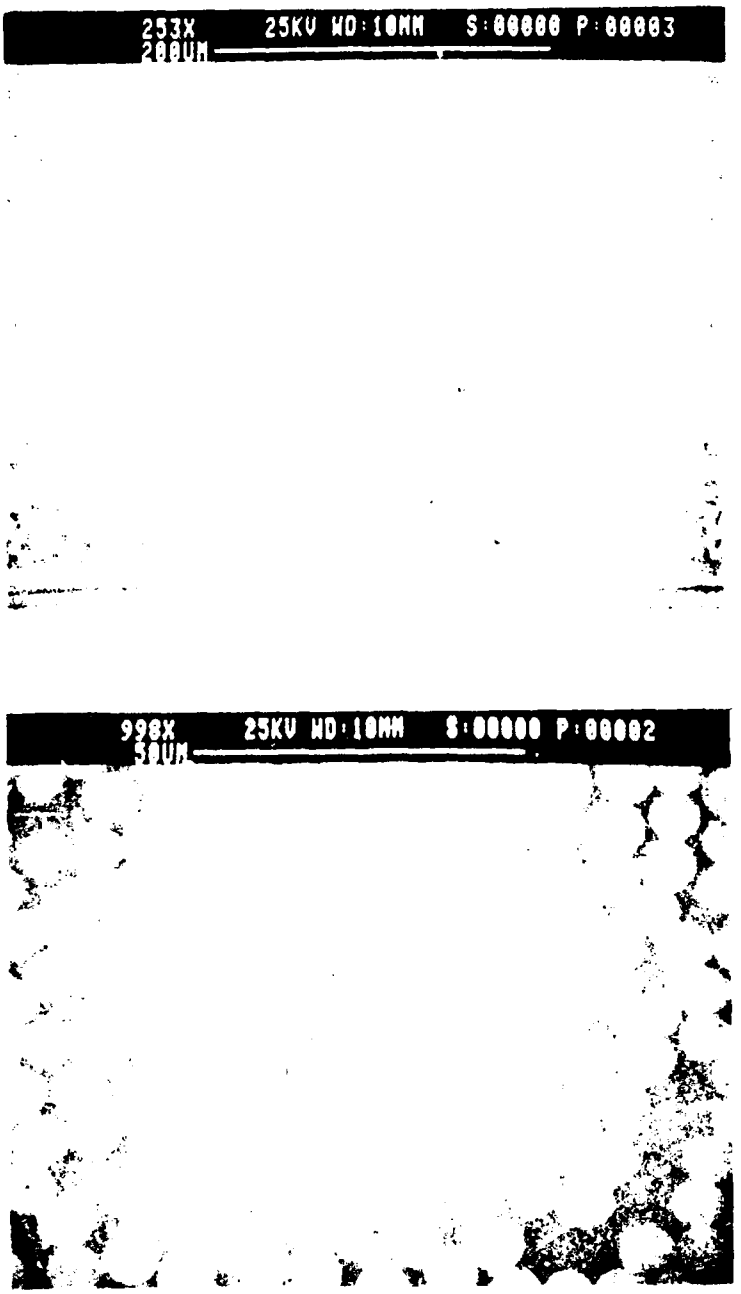


FIGURE 3.5
Photomicrographs of AS4/CATB-49 laminate, 0° view.

Postcure: 4 hr @ 250°C, Layup $(0,90_2,0)_S$

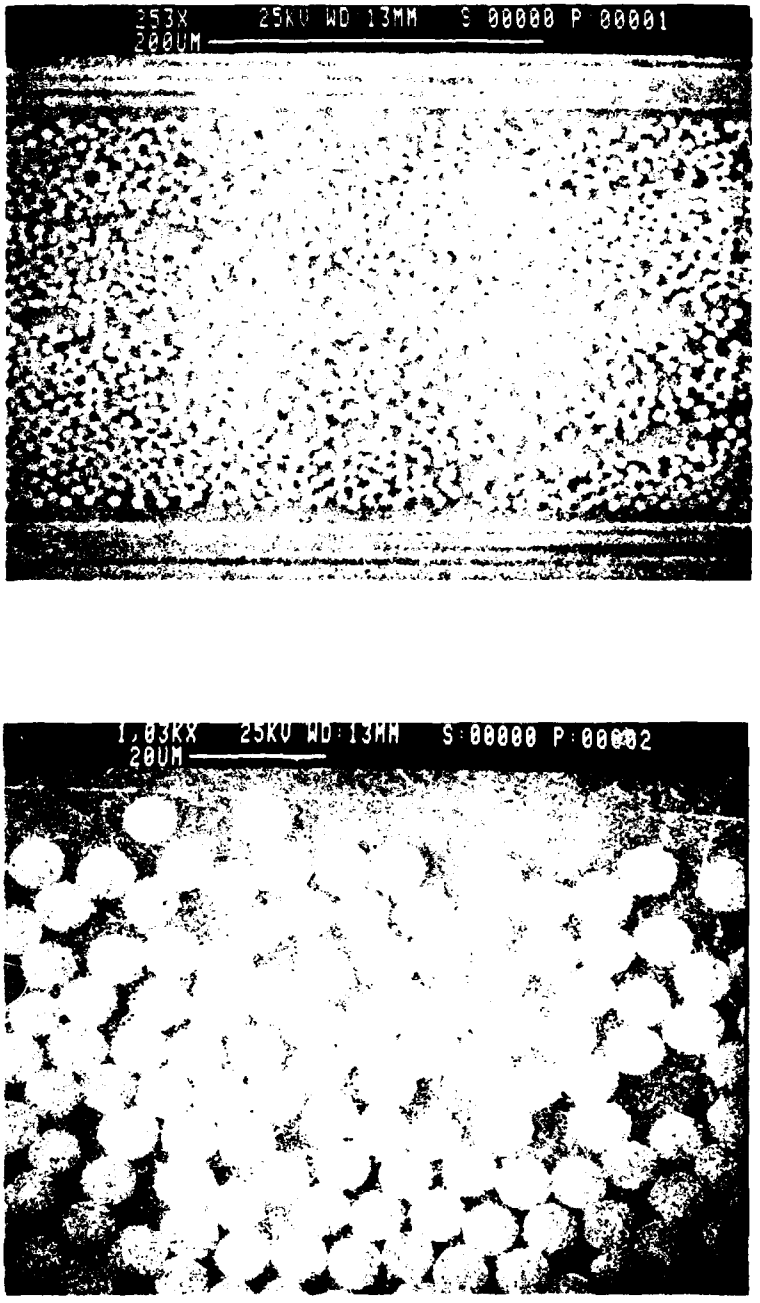
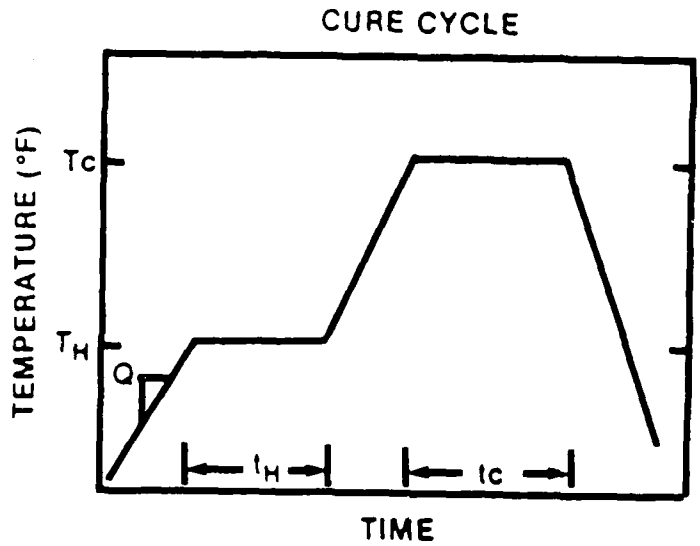


FIGURE 3.6 **Photomicrographs of AS4/CATB-51 laminate, 0° view.**

Postcure: 4 hr @ 250°C, Layup $(0,90_2,0)_S$



SYMBOL	PARAMETER	CYCOM 985 EPOXY	CYCOM 3100 BISMALEMIDE	ATB RESIN FORMULATIONS
Q	Heating Rate	3°C/min	3°C/min	3°C/min
T_H	Hold Temperature	66°C	110°C	150°C
T_C	Cure Temperature	177°C	177°C	177°C
t_H	Hold Time	60 min.	45 min.	90 min.
t_C	Cure Time	120 min	240 min	240 min.
	Pressure	100 PSI	85 PSI	100 PSI
	Postcure Temperature	None	227°C	230°C
	Postcure Time	None	240 min.	240 min.

FIGURE 3.7 ATB RESIN CURE CYCLE DEVELOPMENT

4.0 TASK III: COMPREHENSIVE LAMINATE TESTING

In Task III, the out-times of CATB-44, -49 and -51 prepregs were assessed, laminates were produced, and a wide variety of matrix-dominated mechanical properties were measured. In addition, the effects of thermal spiking and aging were measured. Surfaces of delaminated fracture toughness specimens were examined and the effect of postcure on CATB-44's hot/wet properties was assessed.

4.1 PREPREG OUT-TIME

Gel time and tack adherence of the prepregs were measured as a function of time after exposure to atmosphere at 73°F, 50% RH. The test methods followed are described in Appendix B. The results are presented in Table 4.1.

Gel times for the CATB formulations decreased significantly between the second and third week. CATB-44 decreased in gel time from 507 seconds to 258 seconds between weeks 2 and 3. The corresponding decreases in gel time for CATB-49 and -51 were from 528 seconds to 219 second and from 565 seconds to 262 seconds, respectively. The tack adherence test done at the three week out-time showed undue force (5 psi) is needed to join the CATB-49 formulation, while CATB-44 and -51 adhered at the one psi pressure level considered acceptable.

These evaluations indicated an out-time of two weeks with an outer limit of three weeks.

4.2 LAMINATE FABRICATION

The test laminates that were needed to perform the comprehensive property evaluations shown in Table 4.2, were fabricated from ATB formulations CATB-44, CATB-49 and CATB-51. The stacked prepreg panels were bagged following the no-bleed sequence shown in

TABLE 4.1

CATB FORMULATION PREPREG OUT-TIME

EVALUATION

CATB Formulation	Out-time at 73°F, 50% RH	Gel Time (sec)	Tack Adherence 10 Sec. at 1 psi	5 psi
CATB 44	Initial	609	--	--
	1 week	594	Yes	--
	2 weeks	507	Yes	--
	3 weeks	258	Yes	--
CATB 49	Initial	625	--	--
	1 week	720	Yes	--
	2 weeks	528	Yes	--
	3 weeks	219	No	Yes
CATB 51	Initial	654	--	--
	1 week	645	Yes	--
	2 weeks	565	Yes	--
	3 weeks	262	Yes	--

TABLE 4.2

LAMINATE MECHANICAL PROPERTY TEST MATRIX

TEST TYPE	METHOD	SPECIMEN DIMENSION (IN)	ORIENTATION	NUMBER OF TESTS 73°F DRY	450°F DRY	350°F WET*	425°F WET
0° Flexural Modulus	ASTM D790	.5 x 5	$(0)_{16}$	5	-	5	-
0° Flexural Strength	ASTM D790	.5 x 5	$(0)_{16}$	5	5	5	5
0° Flexural Strain	ASTM D790	.5 x 5	$(0)_{16}$	5	-	5	-
Interlaminar Shear Strength, (4 Point)	AFWAL	.5 x 3	$(0)_{16}$	5	5	5	-
90° Flexural Modulus	ASTM D790	1 X 5	$(90)_{16}$	5	-	-	-
90° Flexural Strength	ASTM D790	1 x 5	$(90)_{16}$	5	-	-	-
90° Flexural Strain	ASTM D790	1 x 5	$(90)_{16}$	5	-	-	-
G_{1c}	NASA 1092-ST5	1.5 x 9	$(0)_{24}$	5	-	-	-
Edge Delamination Strength	AFWAL	1.5 x 10	$(+30_2/-30_2/90_2)_s$	5	-	-	-
In-Plane Shear Modulus	ASTM D3518	1 x 9	$[(\pm 45)_2]_s$	3	-	5	3
In-Plane Shear Strength	ASTM D3518	1 x 9	$[(\pm 45)_2]_s$	3	-	5	3
In-Plane Shear Strain	ASTM D3518	1 x 9	$[(\pm 45)_2]_s$	3	-	5	3

* Wet conditioning = 2 weeks in deionized water at 71°C.

Figure 3.1 and cured in a 19 inch square press mounted autoclave. The previously developed cure cycle shown in Figure 3.7 was used, and the panels were postcured free-standing in a forced air oven for four hours at 230°C (440°F).

To serve as a basis of comparison, three sets of prepregs and laminates were fabricated using the cure cycles shown in Figure 3.7. Laminates of CYCOM 985 (epoxy) on AS-4 fiber, and CYCOM 3100 (BMI) on both AS-4 and IM6 fiber were produced using their standard cure cycles, also shown in Figure 3.7.

Selected laminates were ultrasonically "C" scanned to assess quality. High quality laminates were evidenced by these "C" scans, with no sign of voids or compaction problems.

4.3 MECHANICAL EVALUATIONS

4.3.1 Methods

The laminate mechanical property test matrix developed to evaluate the materials in this program is presented in Table 4.2. Complete descriptions of the test procedures have been provided in Appendix B. The laminate tests that were used to evaluate environmental properties are shown in Table 4.3, along with a referenced methodology.

For the elevated temperature tests, a thermocouple was attached to the specimens. The specimens were then heated to a test temperature of 177°C or 232°C (350°F or 450°F) in 3-4 minutes. For dry tests, the temperature was held for 10 minutes prior to test initiation; for wet tests the temperature was held for 2 minutes prior to test initiation. Wet conditioning consisted of two weeks immersion in water at 71°C (160°F).

TABLE 4.3

LAMINATE ENVIRONMENTAL PROPERTY TEST MATRIX

TEST TYPE	METHOD	SPECIMEN DIMENSION (IN)	ORIENTATION	NUMBER OF TESTS
Tg (Dry)	ASTM D4056	.5 x 2.5	$(90)_{16}$	2
Tg (Wet)*				2
Thermal Spike	General (1) Dynamics	1 x 2	$(0/+45/-45/0)_s$	3
Thermal Aging	General (1) Dynamics	1 x 2	$(0/+45/-45/0)_s$	4

* Wet conditioning: 2 weeks in deionized water at 71°C

(1) L. McKague, Composites for Extreme Environments, ASTM STP-768, 1982

4.3.2 Results

The complete summary table of the comprehensive laminate results is shown in Table 4.4, for both the state-of-the-art materials, and the ATB formulations. These data are discussed below.

Dynamic Mechanical Analysis

Dynamic mechanical profiles were obtained from the $(90^\circ)_{16}$ laminates used for flexure and interlaminar shear determinations. CATB formulations -44 and -51 had slightly higher Tg's than the CYCOM 3100 control on AS-4 fiber. CATB-49 had a slightly lower Tg than the CYCOM 3100 control. The values suggested that the dry laminate mechanical properties would approach the AFWAL target values at elevated temperatures.

0° Flexural Properties

The 0° flexural properties of the AS-4/CATB laminates measured at room temperature/dry conditions were comparable to the AS-4/CYCOM 3100 (BMI) control and significantly exceeded those of AS-4/CYCOM 985 (epoxy) at elevated temperatures. The values approached or exceeded the AFWAL target values. CATB-44 and -51 had slightly better elevated temperature properties than CATB-49, consistent with the DMA results.

The 0° flexure properties of the CATB laminates at 177°C (350°F)/wet are better than the AS-4/CYCOM 3100 laminates; CATB-51 has a 177°C (350°F)/wet flexural strength of 148 ksi which is superior to CYCOM 3100 (126 ksi) and meets the AFWAL target of 150 ksi. CATB-44 and -49 fall between the target and CYCOM 3100 properties.

TABLE 4.4

COMPREHENSIVE LAMINATE EVALUATIONS

Property	Test Temp °F	AT Resin Formulation[a] CATB-44/ AS-4	CATB-49/ AS-4	CATB-51/ AS-4	State-of-the-Art Systems CYCOM® 985/ AS4[b] Lot 806	CYCOM® 3100/ AS4[b] Lot 807	CYCOM® 3100/ IM6 Lot 763	AFWAL Target Value
0° Flexural Strength (KSI)	73	246 ± 16	247 ± 15	259 ± 12	231 ± 18	245 ± 8	253 ± 14	250
	350	186 ± 8	185 ± 8	197 ± 9	152 ± 14	198 ± 16	191 ± 15	200
	450	137 ± 10	122 ± 4	149 ± 13	-	-	-	
	350W	134 ± 5	138 ± 6	148 ± 5	43 ± 5	126 ± 4	121 ± 5	150
	425W	86 ± 4	76 ± 4	80 ± 5	-	-	-	
	450W	62 ± 5	53 ± 2	58 ± 4	28 ± 1	59 ± 2	79 ± 6	-
0° Flexural Modulus (MSI)	73	17.9 ± .5	17.5 ± .4	17.4 ± .6	17.7 ± .3	17.7 ± .7	20.4 ± .2	18.5
	350	17.2 ± .5	17.3 ± .6	16.9 ± .4	17.5 ± .6	17.4 ± .4	20.1 ± .5	-
	450	-	-	-	-	-	-	
	350W	16.7 ± .5	17.2 ± .5	16.8 ± .6	12.3 ± .6	16.3 ± 1.1	18.9 ± .2	-
	425W	-	-	-	-	-	-	
	450W	-	-	-	-	-	-	-
0° Flexural Strain (%)	73	1.38 ± .12	1.41 ± .09	1.48 ± .05	1.30 ± .11	1.38 ± .08	1.24 ± .05	-
	350	1.09 ± .06	1.07 ± .05	1.17 ± .04	0.87 ± .07	1.13 ± .07	0.95 ± .09	-
	450	-	-	-	-	-	-	
	350W	0.80 ± .02	0.81 ± .02	0.88 ± .05	0.35 ± .03	0.77 ± .04	0.64 ± .03	-
	425W	-	-	-	-	-	-	
	450W	-	-	-	-	-	-	-
4 Point Interlaminar Shear Strength (KSI)	73	11.6 ± .4	12.7 ± .6	13.8 ± .3	12.9 ± .4	14.6 ± .4	14.4 ± .4	14
	350	8.5 ± .2	7.9 ± .1	8.3 ± .2	6.2 ± .3	9.6 ± .1	7.9 ± .1	10
	450	6.2 ± .2	4.8 ± .2	5.9 ± .1	-	-	-	
	350W	6.0 ± .1	5.5 ± .3	5.9 ± .1	2.3 ± .2	5.0 ± .1	5.5 ± .1	7.5
	425W	3.8 ± .2	2.9 ± .1	3.3 ± .2	-	-	-	
90° Flex Strength (KSI)	73	10.6 ± .8	10.7 ± .5	10.6 ± 1.0	11.8 ± .6	11.4 ± .6	9.8 ± .5	
90° Flex Modulus (MSI)	73	1.30 ± .03	1.34 ± .01	1.34 ± .04	1.43 ± .05	1.44 ± .04	1.32 ± .01	
90° Flex Strain (%)	73	.82 ± .07	.81 ± .04	.80 ± .09	.86 ± .06	.82 ± .05	.75 ± .03	1.0

TABLE 4.4

COMPREHENSIVE LAMINATE EVALUATIONS

Property	Test Temp °F	AT Resin Formulation[a] CATB-44/ AS-4	CATB-49/ AS-4	CATB-51/ AS-4	State-of-the-Art Systems CYCOM® 985/ AS4[b] Lot 806	CYCOM® 3100/ AS4[b] Lot 807	CYCOM® 3100/ IM6 Lot 763	AFWAL Target Value
G_{IC} (in-lb/in^2)	73	1.43 ± .09	1.12 ± .03	1.19 ± .04	1.55 ± .03	2.56 ± .11*	1.96 ± .06[c]	2.0
Edge Delam. Strength (KSI)	73	21.8 ± .5	21.4 ± .8	21.5 ± .4	29.9 ± 1.2	16.0 ± 1.1	23.6 ± .5	TBD
In-Plane Shear Modulus (MSI)	73	.711	.708	.719	.792	.811	.777	-
	350W	.304±.004	.225±.007	.275±.013	.042±.002	.290±.010	.324±.003	.35
	425W	.134	.085	.102	.034	.116	.171	-
In-Plane Shear Strength (KSI)	73	11.9	11.5	11.0	15.3	13.0	11.8	-
	350W	8.94±.07	7.98±.14	7.78±.11	1.76±.09	8.05±.12	8.15±.12	-
	425W	5.42	4.62	4.10	1.23	4.41	5.91	-
Tg, °F, Tan Delta	Dry	558	514	545	403	541	599	>400
Modulus Int	Dry	469	439	462	365	455	475	
5% Offset	Dry	455	419	442	342	414	457	
Tan Delta	Wet	529	482	514	347	476	554	350-400
Modulus Int	Wet	397	383	396	298	360	428	-
5% Offset	Wet	365	354	361	277	315	412	-
Thermal Spike H_2O Gain (%)	-	0.10	0.06	0.15	0.45	0.48	0.40	<.15
Thermal Aging	Cond 1	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	No
	Cond 2	N.C.	N.C.	N.C.	C.	N.C.	N.C.	Cracking

W = Tested wet after 14 days in H_2O @ 71°F

Note: 0° Flex Strength and Modulus values normalized to 60% fiber volume.

N.C. = No Cracking
C. = Crack Observed

a) AS-4 Unsized Fiber
b) AS-4 "G" Sized Fiber
c) Fiber Bridging

At 232°C (450°F)/wet the 0° flexural strengths of the CATB laminates are comparable to CYCOM 3100's.

Interlaminar Shear Properties

The interlaminar shear properties of the AS-4/CATB laminates measured at room temperature/dry conditions approached those of AS-4/CYCOM 3100 and exceeded those of AS-4/CYCOM 985. They were slightly below the AFWAL target values. A shear failure mode was obtained in all specimens at all conditions, which reinforced the value of the four point shear test in measuring this property. The four point test consistently produced values lower than the three point test of ASTM D2344.

The hot/wet interlaminar shear properties of the CATB formulations showed a significant improvement over the state-of-the-art AS-4/CYCOM 3100 BMI. At 350°F/wet, CATB-44 and -51 had strengths of 6.0 and 5.9 ksi, respectively, while CATB-49 was somewhat lower at 5.5 ksi. These values are compared to the 5.0 ksi for AS-4/CYCOM 3100 and are within 2 ksi of the AFWAL target. The shear strengths of CATB-44, -49 and -51 at 425°F/wet were 3.8, 2.9, 3.3 ksi, respectively.

90° Flexural Properties

The flexural strains to failure of the ATB formulations, measured at 73°F were equal to AS-4/CYCOM 3100. The values were only 80% of the AFWAL target.

Strain Energy Release Rate (G_{IC})

The G_{IC} values obtained on the CATB laminates averaged approximately 1.2 in-lb/in^2. Some fiber bridging was noted, but it was not nearly as severe as seen in the CYCOM 3100 control materials which had a high G_{IC} of 2.5 in-lb/in^2. The presence of fiber bridging precludes a toughness comparison based on these

measurements. The edge delamination and 90° flexural tests are probably more valid indicators of toughness.

Edge Delamination Strength

The edge delamination strengths of the $(+30,-30_2,+30,90_2)_s$ AS-4/CATB laminates were all about 21-22 ksi, a 30% improvement over the state-of-the-art AS-4/CYCOM 3100 but only 72% of the value for AS-4/CYCOM 985 epoxy. From previous experience we have found that edge delamination strength is strongly influenced by the fiber/resin bonding. For example, IM6/CYCOM 3100 edge delamination strength is higher than AS-4/CYCOM 3100. The effect of fiber type on these values was investigated in more detail. The results are given in Section 5.0.

In-Plane Shear Testing

The 350°F/wet shear moduli of CATB-44, -49 and -51 are 0.304, 0.225 and 0.275 Msi. These values compare with the AFWAL target of 0.35 Msi and the AS-4/CYCOM 3100 value of 0.290 Msi. As a percentage of their 23°C/dry shear modulus, both CATB-44 and -51 out-performed AS-4/CYCOM 3100. At 425°F/wet, some material integrity was retained, as reflected in the shear moduli of 0.134, 0.085 and 0.102 Msi for CATB-44, -49 and -51, respectively. AS-4/CYCOM 3100 at 425°F/wet had a shear modulus of 0.116 Msi. IM6/CYCOM 3100 had shear modulus of 0.324 Msi at 350°F/wet and 0.171 Msi at 425°F/wet.

4.4 THERMAL EFFECTS ON MECHANICAL PROPERTIES

4.4.1 Thermal Spike

Three, one-inch by two-inch, specimens $(90/\pm45/0)_s$, from each material were exposed to 71°C, 75% RH for 52 days. Two of these specimens were immersed in 177°C silicone oil for 1 minute every 3.5 days from the start of exposure and returned to 71°C, 75% RH

for a total of 10 cycles. The third specimen was a control, and was not thermally spiked. Moisture gain was measured on all three specimens prior to each thermal spike and at the end of 52 days. Total moisture gain over the course of the test was measured, and comparisons of gain between the control and thermally spiked specimens were made.

The moisture gains of each laminate are compared with their unspiked controls in Figures 4.1 through 4.6. A summary is presented in Figure 4.7.

The CATB control specimens showed an inherently superior resistance to water absorption, with their moisture gains at the end of exposure being 0.70, 0.76 and 0.77% for CATB-49, -44, and -51, respectively. This compared to moisture gains of 1.43, 1.28, and 1.17% for AS-4/CYCOM 985, AS-4/CYCOM 3100, and IM6/CYCOM 3100, respectively.

Additionally, the differences between the moisture gain of the spiked and unspiked CATB formulations met the AFWAL target of <0.15%, with CATB-49, -44 and -51 having differences of 0.06, 0.10 and 0.15%, respectively. AS-4/CYCOM 3100, IM6/CYCOM 3100 and AS-4/CYCOM 985 all failed to meet the AFWAL target with differences of 0.48%, 0.40% and 0.45%, respectively. This effect is seen as a combination of two beneficial ATB formulation attributes: their inherently lower moisture pick-up, coupled with an increased resistance to cracking during spiking.

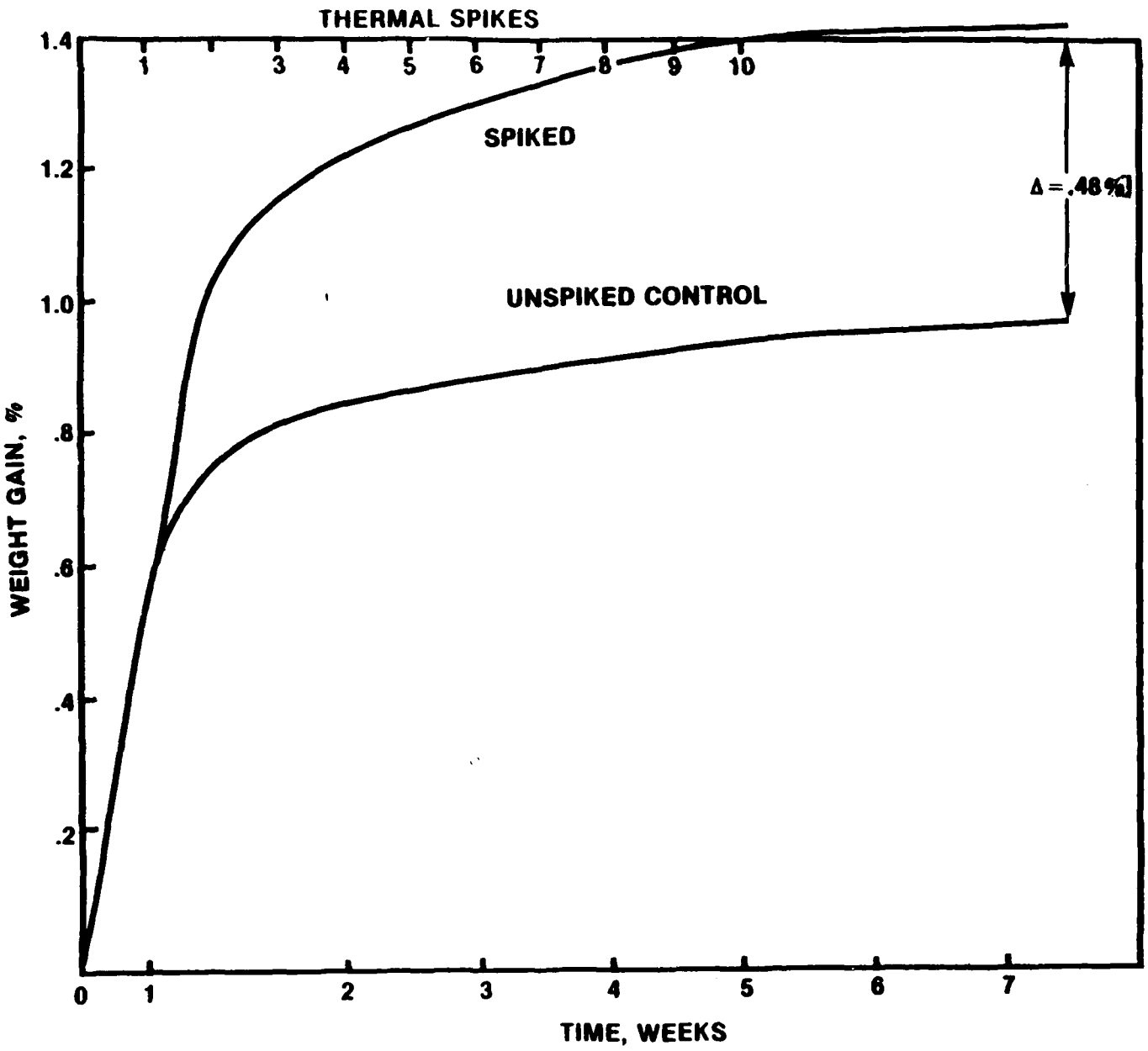


FIGURE 4.1
THERMAL SPIKING RESULTS: CYCOM 985/AS4

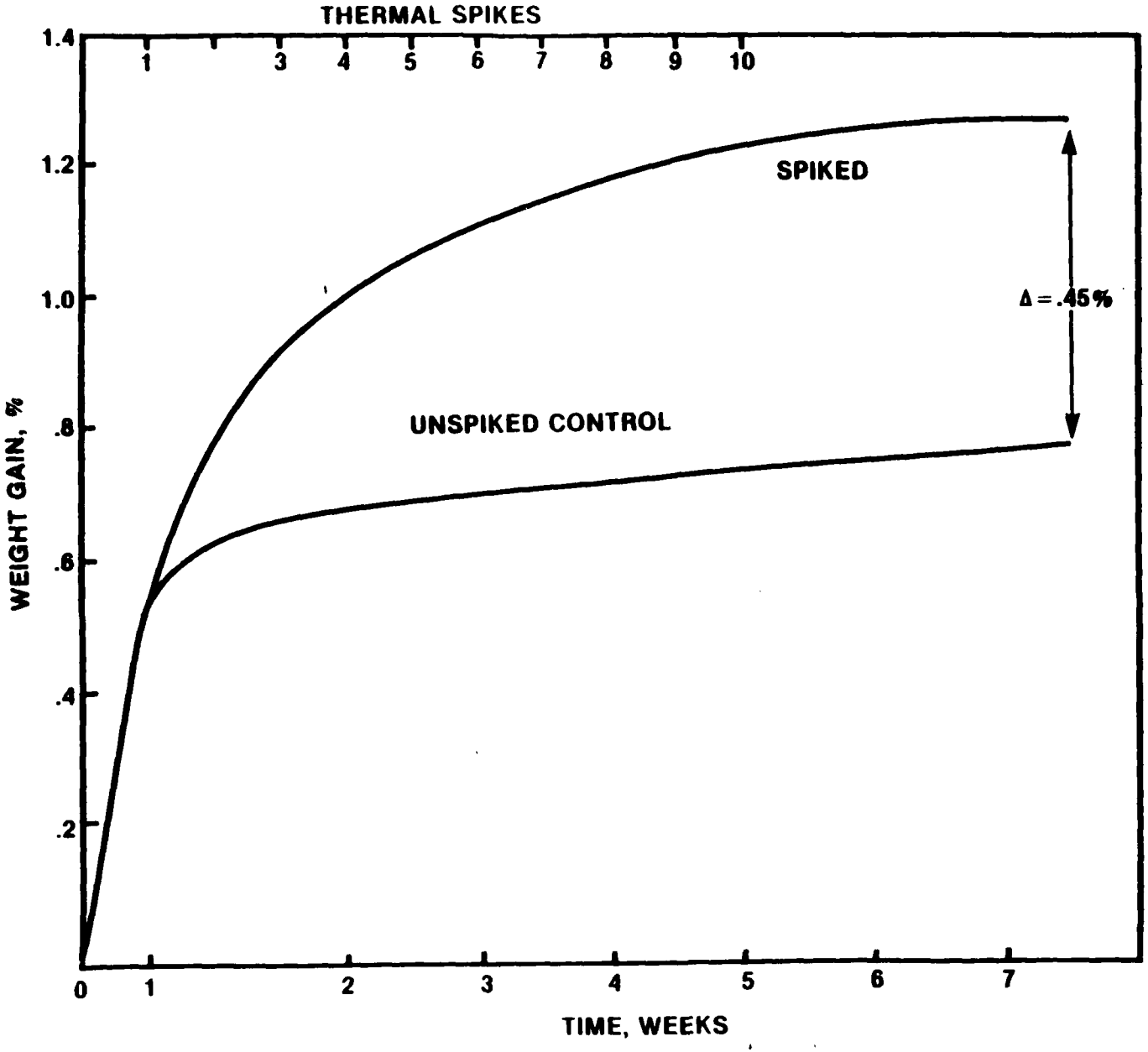


FIGURE 4.2
THERMAL SPIKING RESULTS: CYCOM 3100/AS4

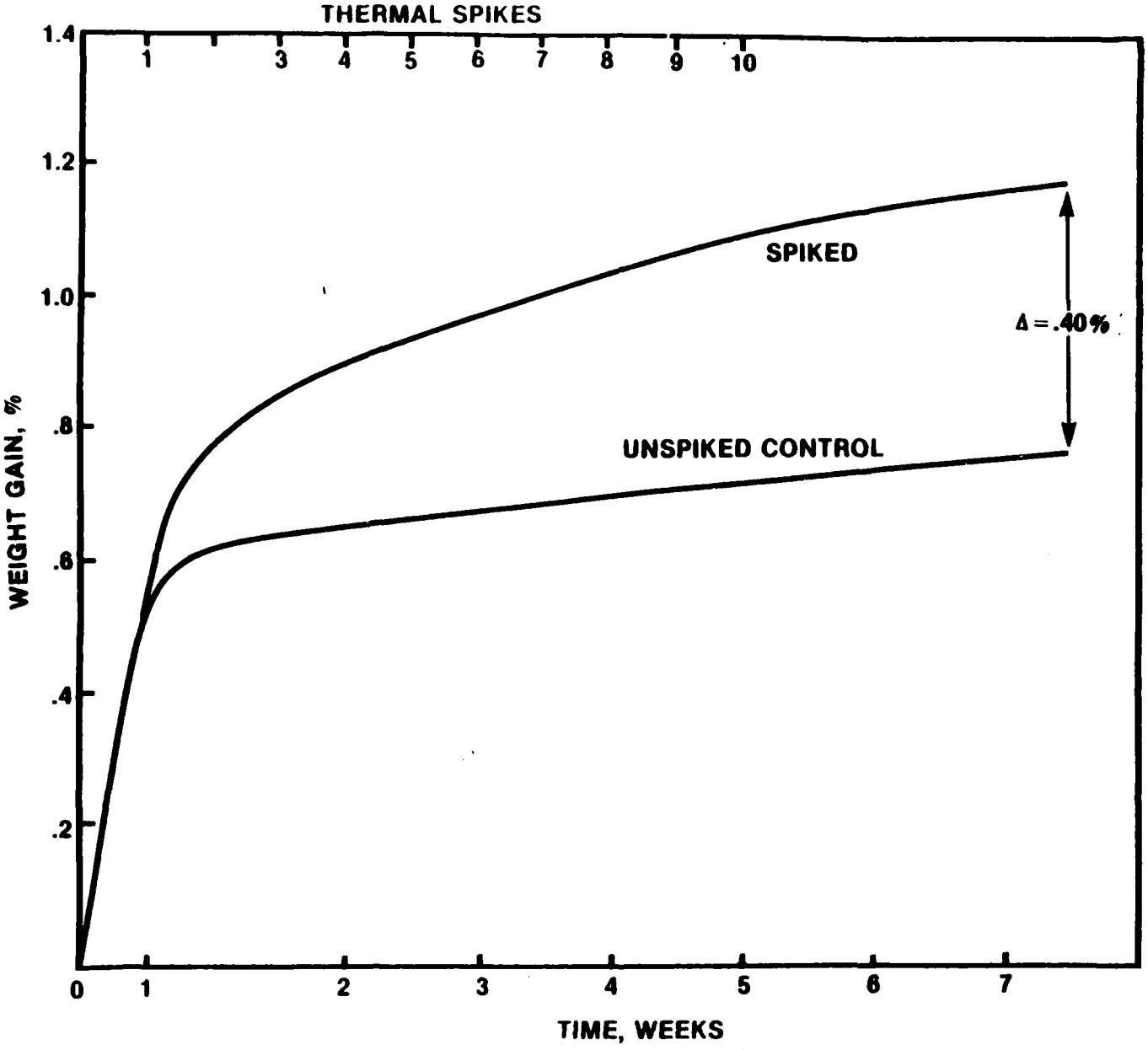


FIGURE 4.3
THERMAL SPIKING RESULTS: CYCOM 3100/IM6.

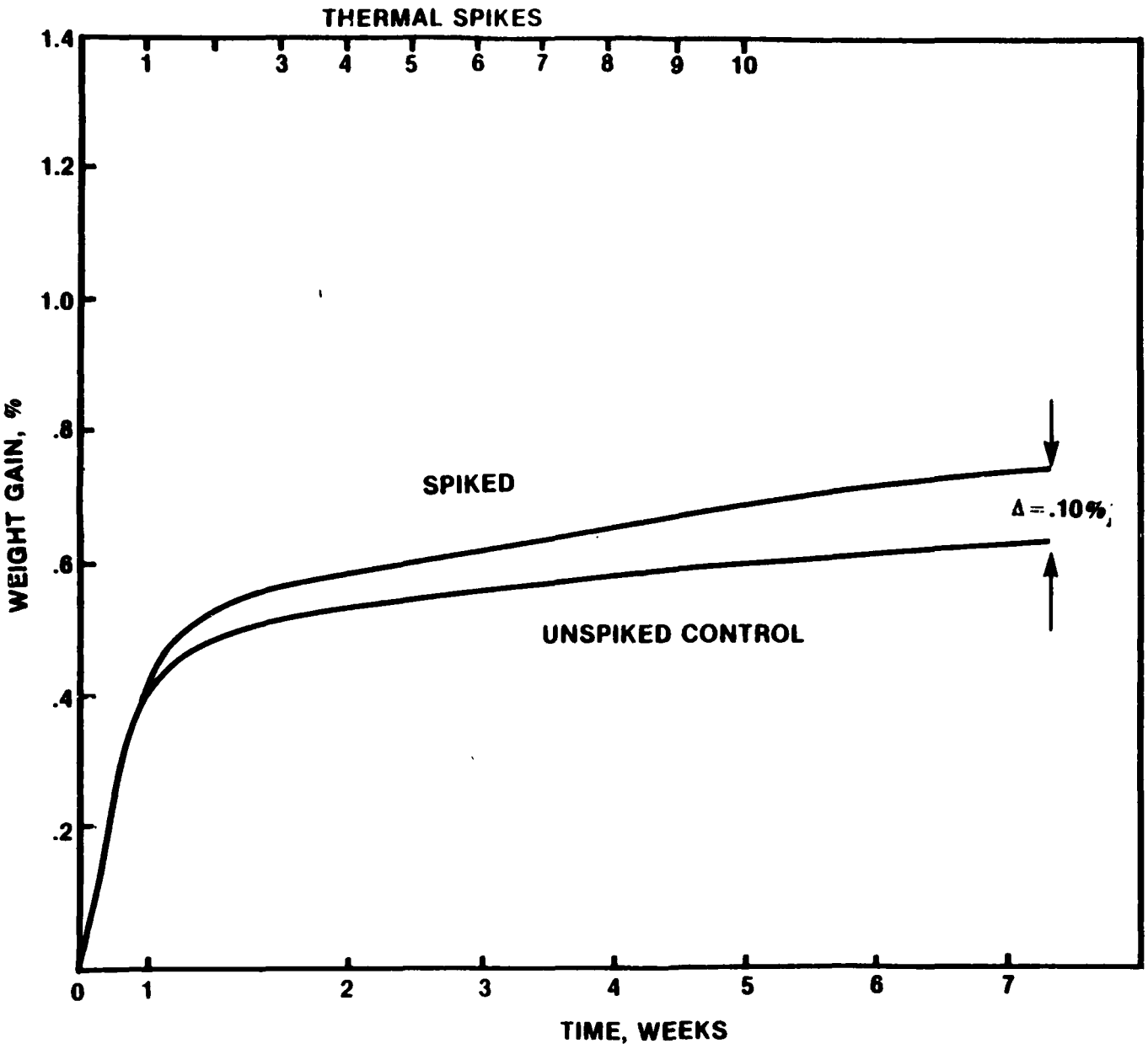


FIGURE 4.4
THERMAL SPIKING RESULTS: CATB-44/AS4

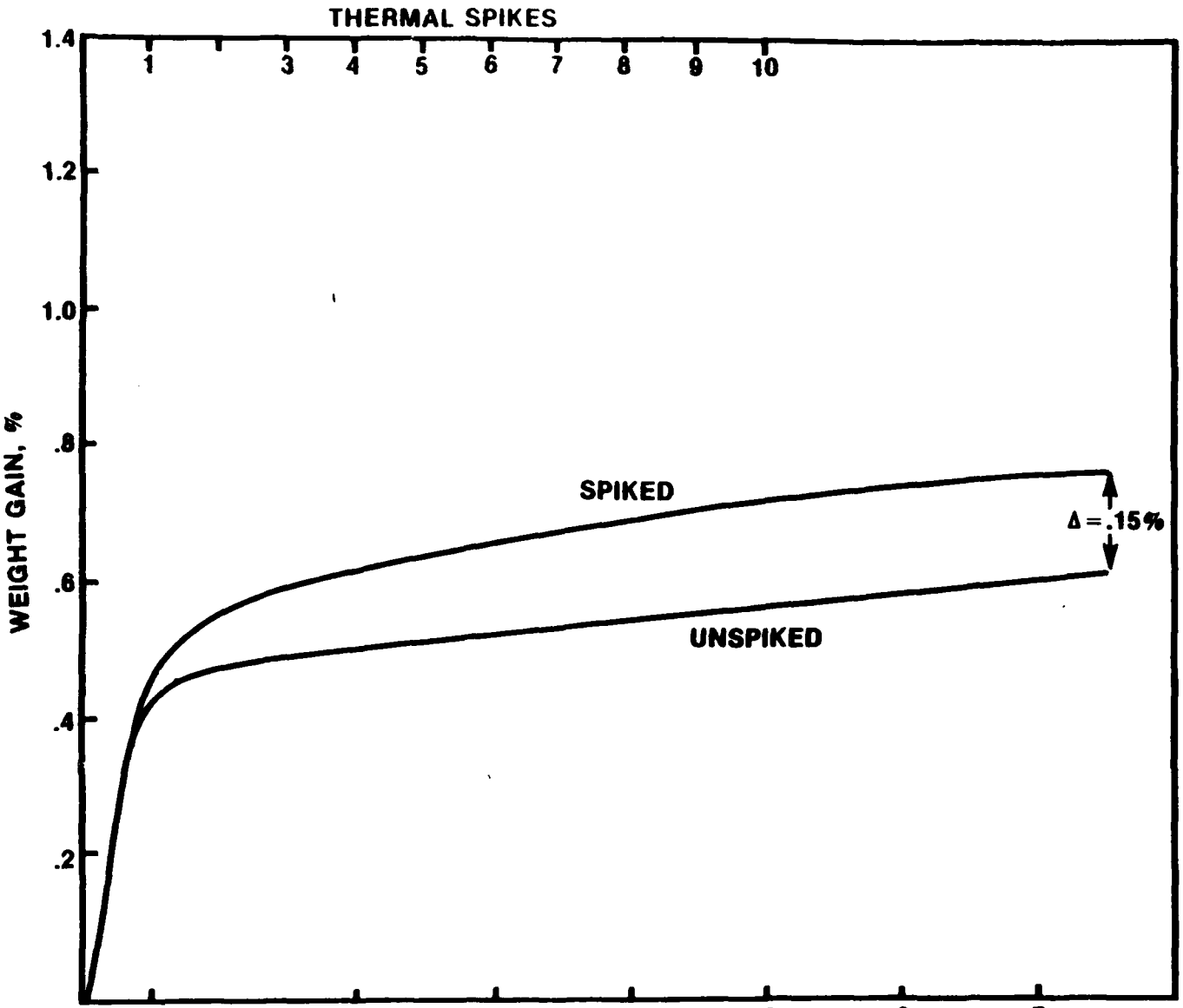


FIGURE 4.5
THERMAL SPIKING RESULTS: CATB-51/AS4

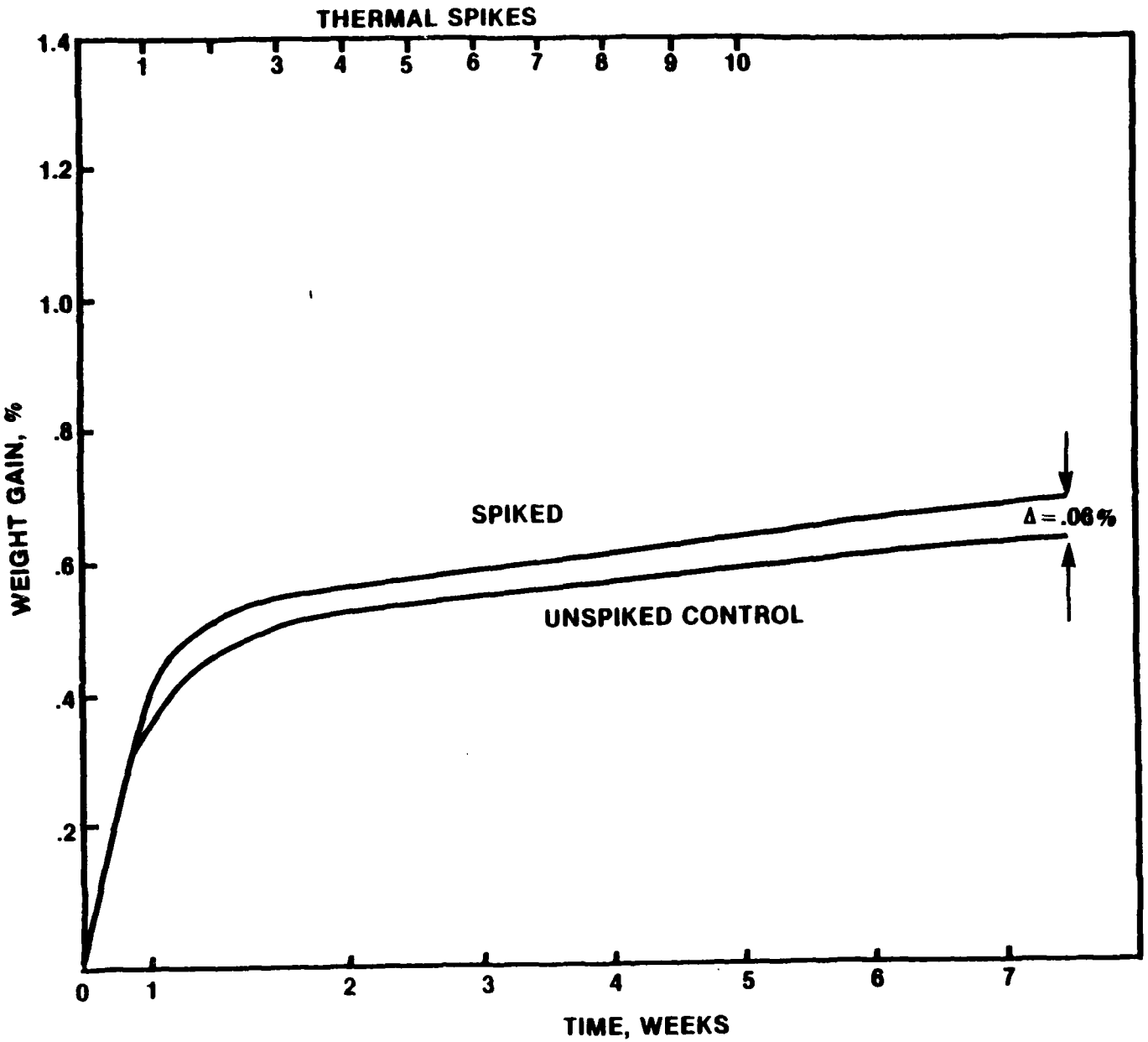


FIGURE 4.6
THERMAL SPIKING RESULTS: CATB-49/AS4

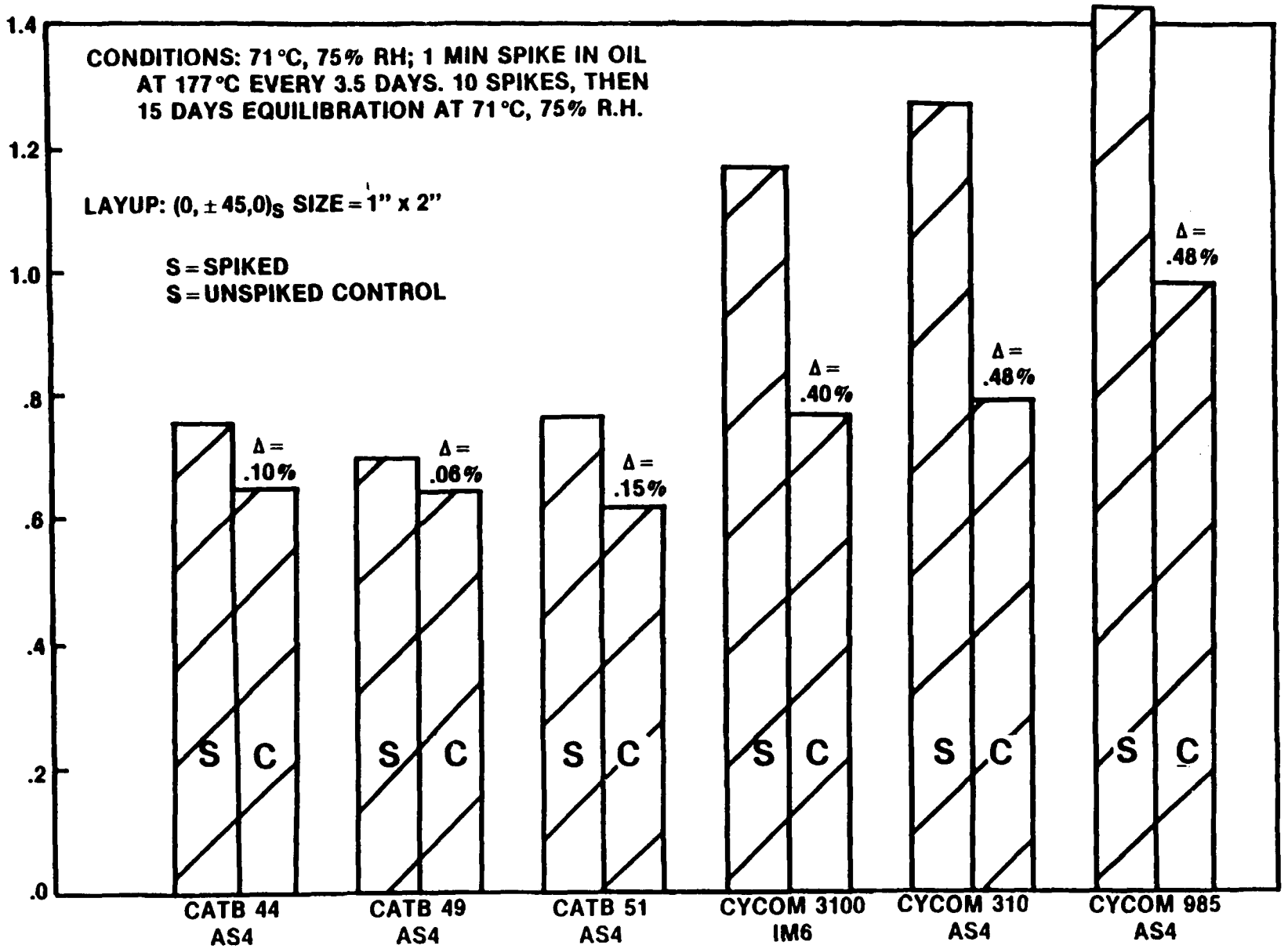


FIGURE 4.7 THERMAL SPIKE H_2O GAIN, CATB AND CONTROL MATERIALS

4.4.2 Thermal Aging Tests

Four, one-inch by two-inch specimens, $(0/\pm 45/0)_s$, were subjected to thermal aging, two specimens of each material at the following conditions:

Condition I

- Exposed for 25 hours at 350°F, then
- Exposed for 264 hours at 275°F

Condition II

- Exposed for 25 hours at 450°F, then
- Exposed for 264 hours at 275°F

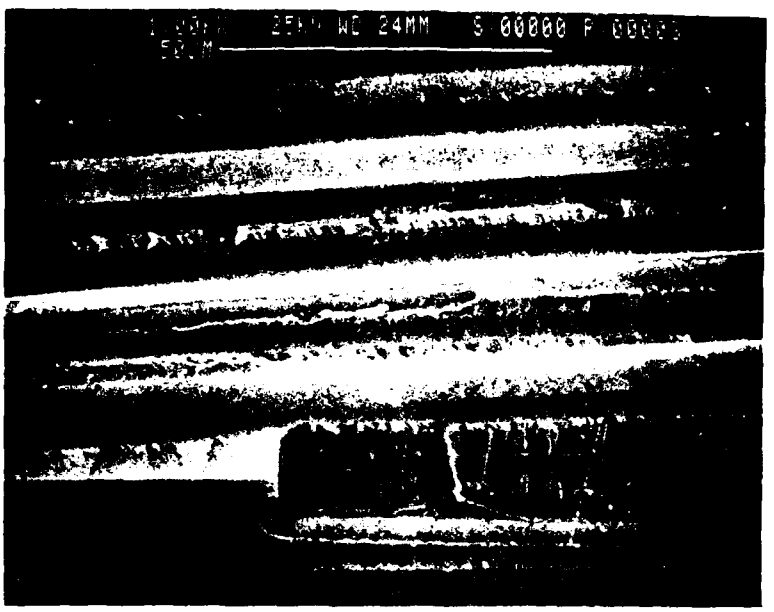
Following these exposures, the specimen edges were polished and inspected for microcracking using 250 to 500x photomicrographs.

None of the CATB formulations showed any microcracking or resin-fiber debonding after aging under either condition. The two CYCOM 3100 laminates did not microcrack or debond. The CYCOM 985 laminate, aged at Condition II, had one crack through the center plies when viewed in the 90° direction.

4.5 FRACTURE SURFACE ANALYSIS OF G_{IC} SPECIMENS

Photomicrographs of the failure surfaces of the G_{IC} strain energy release rate specimens were made to assess differences in the failure modes between the CATB and control laminates. The predominant difference noted was the degree of fiber/matrix debonding. The epoxy laminate, AS-4/CYCOM 985, shown in Figure 4.8, had a large degree of matrix cracking with a moderate amount of fiber/matrix failure. The CATB materials and the CYCOM 3100

250 X



1000 X

FIGURE 4.8
G_{IC} FRACTURE SURFACE
CYCOM 985/AS-4 LOT 806

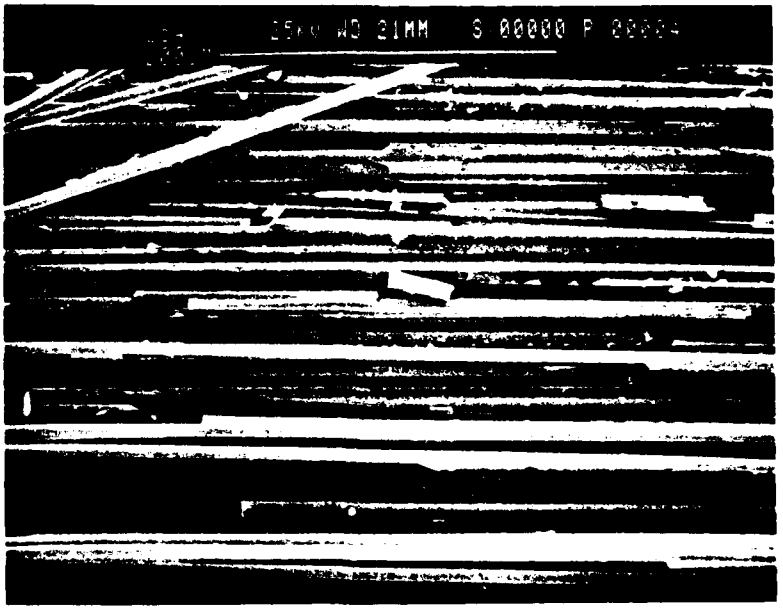
control had large amounts of bare fiber and grooves in the resin that had held fibers. An example is shown in Figure 4.9. CATB and 3100 had cracked predominantly at the fiber/matrix interface. This suggested that improvement in composite properties might be obtainable with improvements in the interface, i.e., a change in the fiber.

4.6 EFFECTS OF POSTCURE ON HOT/WET MECHANICAL PROPERTIES

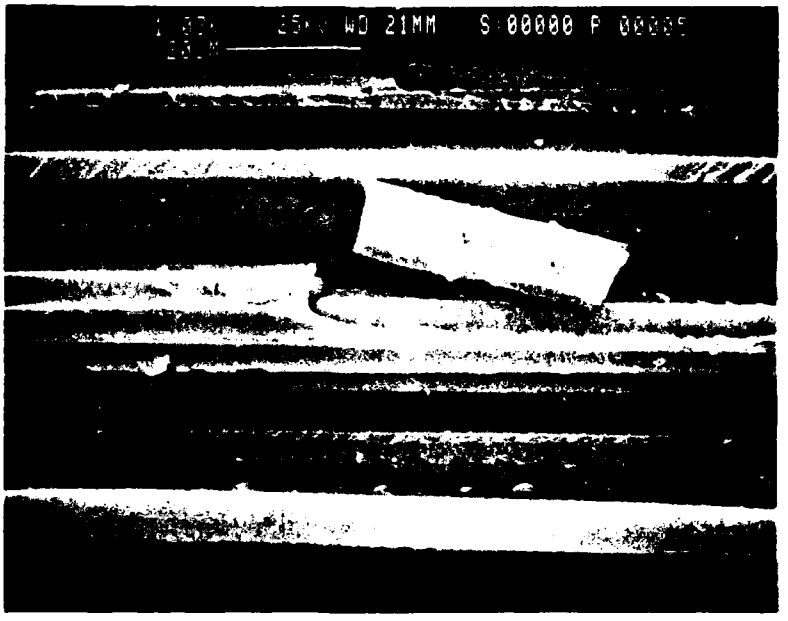
To determine if a higher temperature postcure would enhance the hot/wet performance of CATB-44, a second 16-ply unidirectional laminate was laid up and cured using the previously established procedures. Upon completion of the cure cycle, the laminate was unbagged and postcured free-standing in a circulating air oven at 250°C (480°F) for 4 hours. 0° flexure and 4 point interlaminar shear specimens were conditioned for two weeks in water at 71°C. Tests were carried out at 177°C (350°F), 218°C (425°F) and 230°C (450°F). The results, comparing the properties of laminates post-cured at 230°C (440°F) and 250°C (480°F) are reported in Table 4.5.

The hot/wet mechanical properties of CATB-44 were signifi-cantly improved when the laminate was postcured at 250°C (480°F). Flexure strength increased 20% at 350°F/wet, 33% at 425°F/wet and 58% at 450°F/wet, compared to the standard 230°C (440°F) postcure. Four point interlaminar shear strength increased 10% at 350°F/wet and 20% at 425°F/wet. The 350°F/wet flexural strength of CATB-44 postcured at 250°C (480°F), 161 ksi, exceeded the AFWAL target of 150 ksi.

While the beneficial effects of a 250°C (480°F) postcure on the hot/wet uniaxial mechanical properties of CATB-44 were clear, previous work on postcuring had indicated that some resin/fiber debonding might result from a 250°C (480°F) postcure. However, by changing the fiber and/or surface treatment to obtain a better bonding, it was thought that it would be possible to use this



250 X



1000 X

FIGURE 4.9
G_{IC} FRACTURE SURFACE
CATB 51

TABLE 4.5

EFFECT OF POSTCURE TEMPERATURE ON CATB-44 LAMINATE HOT/WET PROPERTIES

Property	Units	Test Temperature °F	CATB-44/AS4 PC 4 Hr at 230°C	PC 4 Hr at 250°C	AFWAL Target
0° Unidirectional Flexural Strength	KSI	350°F/Wet	134±5	161±15	150
	KSI	425°F/Wet	86±4	113[a]	-
	KSI	450°F/Wet	62±5	98[a]	-
4 Point Interlaminar Shear Strength	KSI	350°F/Wet	6.0±.1	6.6±.1	7.5
	KSI	425°F/Wet	3.8±.2	4.6±.1	-

(a) = average of three specimens
Wet = 14 dats in D.I. H_2O at 71°C

postcure temperature to improve hot/wet performance.

4.7 RECOMMENDATIONS

CATB-44 had the best high temperature properties while having comparable or superior toughness properties when compared to CATB-49 and -51. It was therefore recommended and approved for further study and optimization in Task IV.

5.0 TASK IV: FULL SCALE PREPREG PRODUCTION

Because formulations using m-ATS were found to offer no advantage over those containing m-ATB, and because they had less tack, a change in the program was recommended to, and approved by, AFWAL. The modification included reducing the amount of work done on further m-ATS formulations and expanding the evaluation and optimization of a m-ATB formulation. The enlarged Task IV included: heat aging of CATB-44 neat resin, the effect of fiber on CATB-44 laminate properties, full-scale prepreg production, and the evaluation of interleaf technology in CATB-44 laminates.

5.1 CATB-44 NEAT RESIN HEAT AGING

As part of the expanded investigations of the properties of CATB-44 matrix resin, the effect of heat aging on the mechanical properties of CATB-44 was assessed.

Heat Aging Protocol

CATB-44 neat resin castings were prepared, aged in a circulating air oven at 400°F for periods of 0, 24, 50, 100 and 200 hours and their mechanical properties compared to assess the effects of the aging.

Five castings, 5 inches by 4 inches by 1/16 inch, were cured and postcured using the cure cycle:

1.5 hours at 150°C (300°F)
4 hours at 177°C (350°F)
Postcure 4 hours at 250°C (480°F)

The 0 hour control casting was stored in a desiccator to retain its dry state. Each of the aged castings was desiccated upon removal from the aging oven. Test specimens for flexure,

fracture toughness, and dynamic mechanical analysis were prepared and the evaluations made on each casting. The test matrix is shown in Table 5.1.

Aging Results

The results of the heat aging study are presented in Table 5.2. No detrimental effect of heat aging at 400°F on the flexural properties or fracture toughness of CATB-44 was seen over the 200 hour exposure period. The resin Tg increased gradually with aging exposure, from 250°C (482°F) unaged, to 271°C (520°F) after the 200 hour aging period. This increase was significant, and because Tg is an indicator of upper end-use temperature, it was considered a beneficial effect.

5.2 INFLUENCE OF FIBER TYPE ON CATB-44 PROPERTIES

The expanded investigation of CATB-44 composites focused primarily on the possibility of composite performance improvement through the choice of fiber reinforcement. Five commercially available, sized carbon fibers were used to prepare test laminates with CATB-44 as the matrix resin. The goal was to identify fibers having superior fiber/matrix adhesion to that obtained with Hercules AS-4 fiber, the fiber used in previous evaluations in this program. Improved fiber/resin adhesion was expected to result in an increase in composite toughness and shear/transverse strength. Increased adhesion would also suppress interface related "microcracking" during laminate postcure, allowing a higher postcure temperature to be used, thus enhancing composite hot and hot/wet performance.

5.2.1 Resin Master Batch Preparation and Film Coating

One four-pound batch of CATB-44 resin was produced. HPLC analysis confirmed the correctness of formulation and the absence of cure advancement. The resin was stored at 0°F prior to film

TABLE 5.1

Test Matrix for CATB 44 Neat Resin Heat Aging Study

Test	Method	Test Conditions	Number of Replicates
Flexural Strength, Modulus, Strain	ASTM D790	73°F, Dry	5
Compact Tension Fracture Toughness	ASTM E399 Mod.	73°F, Dry	5
Tg by DMA	ASTM D4056	Dry	1

TABLE 5.2

EFFECT OF HEAT AGING ON CATB 44 NEAT RESIN CASTING PROPERTIES

Aging Condition	Flexural Strength (KSI)	Flexural Modulus (MSI)	Flex Strain to Break (%)	K_{ic} Fracture Toughness (PSI-in 1/2)	Tg, °F by DMA Modulus Intersect
None, as cured	19.6 ± 1.2	0.629 ±0.003	3.4 ±0.2	680 ± 20	482
24 Hours at 400°F	19.2 ± 0.2	0.621 ±0.004	3.5 ±0.4	730 ± 40	495
50 Hours at 400°F	20.0 ± 2.3	0.607 ±0.002	3.6 ±0.4	670 ± 30	507
100 Hours at 400°F	18.0 ± 3.8	0.623 ±0.004	3.2 ±0.6	730 ± 40	505
200 Hours at 400°F	19.6 ± 0.9	0.613 ±0.007	3.5 ±0.2	730 ± 60	520

AGING: CIRCULATING AIR OVEN ± VALUES ARE 90% C.L.

coating.

Film coating on release paper was accomplished on our lab-scale film coater, which consists of two parallel circular stainless steel bars. The spacing between the bars is adjustable so that film thickness and weight can be controlled. The upper bar is fitted with cartridge heaters to control the temperature and thereby the viscosity of the resin during the coating operation. This allows the production of resin films with constant thickness and areal weight.

One hundred linear feet of 12-1/2 inch wide, resin coated release paper were manufactured using the following procedure:

1. Both the resin and the heated bar were preheated to 110°C.
2. The coater gap was set at 0.0075" and the beginning of a roll of ca. 0.005" thick silicone release paper was fed through the gap.
3. The preheated resin was slowly poured onto the junction of the upper, heated bar and the incoming release paper.
4. The paper was pulled through the coater at a rate of approximately 5 feet per minute while resin was poured slowly onto the back side of the steel bars, maintaining a supply of resin.
5. The coated paper was cut into 56 inch lengths and the resin areal weight determined on each length.

Twenty pieces of resin film were identified that had areal weights between 72 and 80 grams/meter^2. This resin areal weight, when combined with fibers at an areal weight of 145 grams/meter^2 would produce prepreg with a resin content of 34$\pm$2%.

5.2.2 Prepreg Preparation

Five commercially available, sized fibers were recommended

and approved for this study after discussion with the Project Engineer. These fibers were:

Amoco's	Thornel T300, UC309 sized
Amoco's	Thornel T500, UC309 sized
Amoco's	Thornel T40, UC309 sized
Hercules'	Magnamite AS-4, "G" sized
Hercules'	Magnamite IM7, "G" sized

The manufacturers' reported fiber properties are presented in Table 5.3. These fibers were chosen to compare the CATB-44 laminate mechanical properties on the basis of 1) fiber manufacturer and, thereby, surface treatment, and 2) fiber modulus.

Sixteen square feet of prepreg, Grade 145, with a resin content of 34±2% was produced from each fiber in the following manner:

1. A 52 inch length of 12 inch wide resin coated release paper was laid down on the assembly bench and taped in place at the ends.
2. Single tows of fiber were laid down parallel to each other, under slight tension, at the spacing indicated in Table I to produce a fiber areal weight of 145 grams/meter^2.
3. The assembly was covered with ARMALON® release material (TEFLON® coated fiberglass cloth) and the tows tacked in place with a hot iron.
4. The assembly was transferred to a hot table set at 110°C and rolled parallel to the fibers until tow spreading and wetting were accomplished.
5. Steps 1 through 4 were repeated three times for each fiber.

The resultant prepreg was then stored at 0°F until laminate fabrication.

TABLE 5.3

SELECTED FIBER/TOW ATTRIBUTES -- CATB 44 FIBER INFLUENCE STUDY

PROPERTY/ATTRIBUTE	UNITS	AMOCO			HERCULES	
		T-300	T-500	T-40	AS4	IM7
Fiber Diameter	Microns	7	7	6	8	5
Tensile Strength	KSI	450	530	820	520	800
Tensile Modulus	MSI	33	35	41	34	44
Tensile Failure Strain	%	1.30	1.50	2.0	1.53	1.86
Fiber Density	g/cm^3	1.73	1.79	1.81	1.80	1.78
12K Tow Yield	g/m	0.806	0.780	0.447	0.877	0.445
Tow Spacing for Grade 145	tows/in.	4.56	4.72	8.24	4.20	8.28
Fiber Shape	--	Irr.	Irr.	Irr.	Circular	Circular
Fiber Topography	--	Striated	Striated	Striated	Smooth	Smooth

5.2.3 Laminate Fabrication

Three test laminates were fabricated from each CATB-44/fiber prepreg. The laminates sizes and orientation are shown in Table 5.4.

The laminates were bagged without bleeders following the procedure established for ATB laminates. The autoclave cure cycle used for these laminates differed from the cycle used in our earlier laminate evaluations only in postcure temperature, which was raised from 230°C to 250°C in order to increase the hot/wet performance of the material. The postcure was carried out in a circulating air oven with the laminates unrestrained.

5.2.4 Laminate Evaluation

Test Methods

The test methods chosen for this study along with the test matrix are shown in Table 5.5. The 0° compression evaluations, performed both dry and wet at both room and elevated temperatures, were chosen as a measure of the laminate's hot/wet performance. Edge delamination and compression interlaminar shear (CILS) measurements were chosen to determine improvements in laminate properties due to fiber type or fiber-resin adhesion improvement. Dynamic Mechanical Analysis (DMA) was chosen as a means of determining the cure state of the laminates.

In addition to these evaluations, laminate quality was assessed by microscopic observation of laminate cross-sections, and resin contents were measured. SEM observations of the CILS fracture surfaces were made to qualitatively assess fiber-matrix adhesion.

TABLE 5.4

TEST LAMINATES FABRICATED FOR FIBER EFFECT STUDY USING CATB 44 RESIN

LAMINATE NUMBER	ORIENTATION	SIZE	EVALUATION
1	$(0°)_8$	4"(0°)x12"	0° Compression Strength
2	$(0°)_{30}$	5"(0°)x4"	Compression Interlaminar Shear Strength Dynamic Mechanical Analysis Fractography Resin Content
3	$(\pm 25_2, 90)_s$	12"(0°)x6"	G.D. Edge Delamination - Stress at First Crack

TABLE 5.5

LAMINATE FIBER-RESIN ADHESION TEST MATRIX

Test Type	Method	Specimen Dimensions (in)	Orientation	Number of Tests 73°F Dry	73°F Wet*	450°F Dry	350°F Wet*
0° Compression Strength	Boeing BMS-8-212E	3.15x0.5	$(0)_8$	5	5	5	5
Compression Interlaminar Shear Strength	ASTM D3846	3.15x0.5	$(0)_{30}$	5			
Edge Delamination Strength	General Dynamics B-009	12x1	$(\pm 25_2 90)_s$	5			
Tg by DMA	ASTM D4056	0.5x2.5	$(90)_{30}$	1			

* Wet conditioning = 14 days in deionized water at 71°C

The results of the study of fiber influence on CATB-44 laminates are given in Table 5.6.

Laminate Quality

Polished cross-sections of the $(0)_{30}$ laminates were examined for resin distribution and void formation. A satisfactory level of resin distribution along with minimal void content was indicated.

Resin Content

Due to the low void levels observed, laminate density measurements were used to determine approximate laminate resin content. Knowing the density of the fibers and CATB-44 neat resin, resin contents were calculated using the following formulae:

1) $$RC_V = \frac{D_F - D_L}{D_F - D_R} \times 100$$

where: RC_V = resin volume %
D_F = fiber density in g/cm^3
D_L = laminate density in g/cm^3
D_R = resin density in g/cm^3

2) $$RC_W = \frac{RC_V \times D_R}{D_L}$$

where: RC_W = resin weight %

The laminate density was determined on 3 gram pieces of the $(0°)_{30}$ laminates by the Archimedes Method with isopropanol as the immersing liquid. The measured resin contents were all in the

TABLE 5.6

ATB FIBER-RESIN INTERFACE STUDY TEST RESULTS

PROPERTY	UNITS	TEST CONDITIONS	CATB-44 ON: T-300 309 SIZE	T-500 309 SIZE	AS4 "G" SIZE	T-40 309 SIZE	IM7 "G" SIZE
0° Compression Strength	ksi	73°F Dry	206±12	214±17	210±25	222±6	209±7
		73°F Wet	193±20	173±15	195±16	212±17	210±7
		450°F Dry	132±10	139±5	142±16	156±7	148±7
		350°F Wet	115±4	116±3	120±8	123±3	135±7
Compression Interlaminar Shear Strength	ksi	73°F Dry	9.23 ±0.47	8.74 ±0.57	8.04 ±0.36	8.40 ± 0.33	8.90 ±0.96
$(0°)_{30}$ Laminate Resin Content	%	--	31.5	34.0	32.2	34.5	34.5
G.D. Edge Delamination Strength, Crack	ksi	73°F Dry	24.8±1.2	23.5±1.0	18.3±.6	19.6±.7	21.4±2.5
Tg by DMA:							
tan	°F	Dry	573	568	577	561	565
Modulus Int.			500	496	507	491	487
5% offset			473	469	479	457	466

All laminates post cured 4 hours at 250°C
Wet = 2 weeks in H_2O @ 71°C
Mechanical properties are an average of 5 specimens
± values are 90% confidence limits

range of 33±2% by weight.

Dynamic Mechanical Analysis

In order to assess any fiber or sizing effect on the cure state of the CATB-44 laminates, DMA profiles were obtained from each $(0°)_{30}$ laminate. The specimens, 0.4 by 2.5 inches (90°), were run on the DuPont 982 DMA at a heating rate of 5°C/minute from 23°C to Tg+50°C.

The DMA Tg results are shown in Table 5.6. These results indicated that all of the test laminates had achieved a similar cure state, unaffected by any fiber treatment or sizing difference.

Compression Interlaminar Shear Strength

Five replicate specimens from each $(0°)_{30}$ laminate were tested at room temperature following the procedures outlined in ASTM D3846. The test specimen is shown in Figure 5.1.

Small differences in shear strength were measured for the CATB-44 laminates, with the T300/CATB-44 laminate being the highest at 9.2 ksi and the AS-4/CATB-44 laminate the lowest at 8.0 ksi. Complete results are shown in Table 5.6 and Figure 5.2.

Edge Delamination Strength

Five replicate specimens from each $(\pm 25_2, 90)_s$ laminate were evaluated at room temperature. The specimens were 12 inches in length, one inch in width and were tested at a speed of 0.05 inches per minute. The specimen edges were painted with white ink to assist in the detection of crack initiation.

Significant differences in edge delamination strength were measured. The T300/CATB-44 and T500/CATB-44 laminates showed the

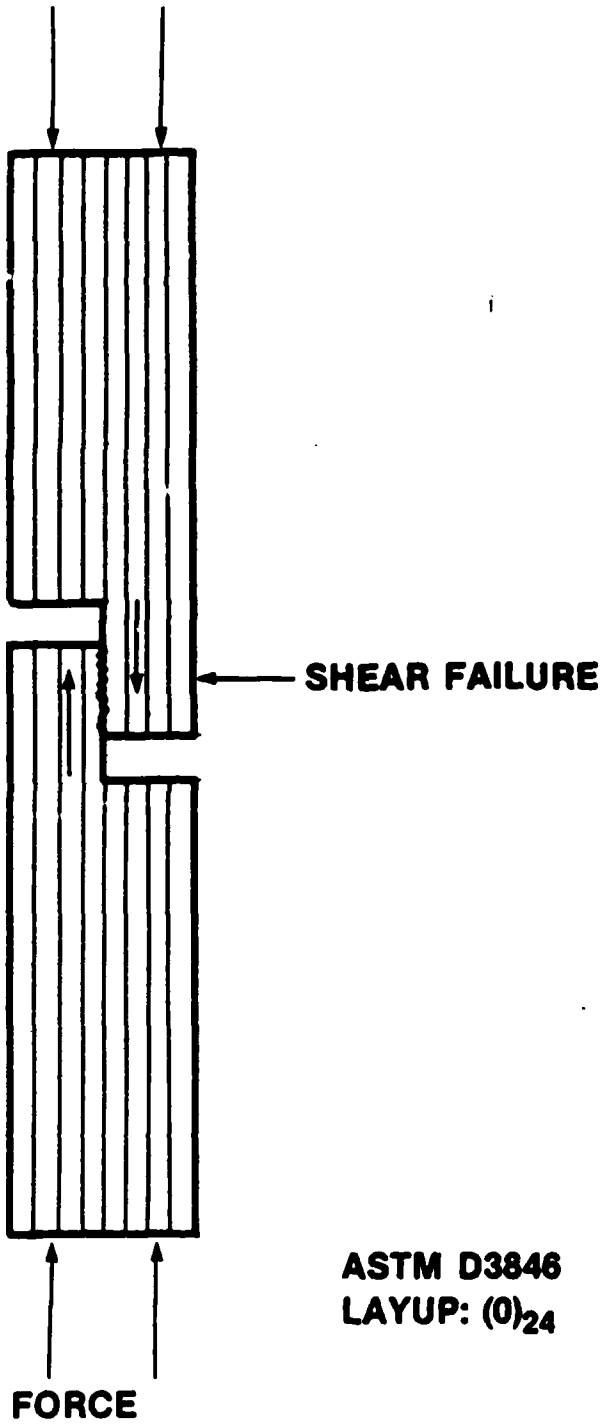


FIGURE 5.1 COMPRESSION INTERLAMINAR SHEAR TEST (CILS) SPECIMEN

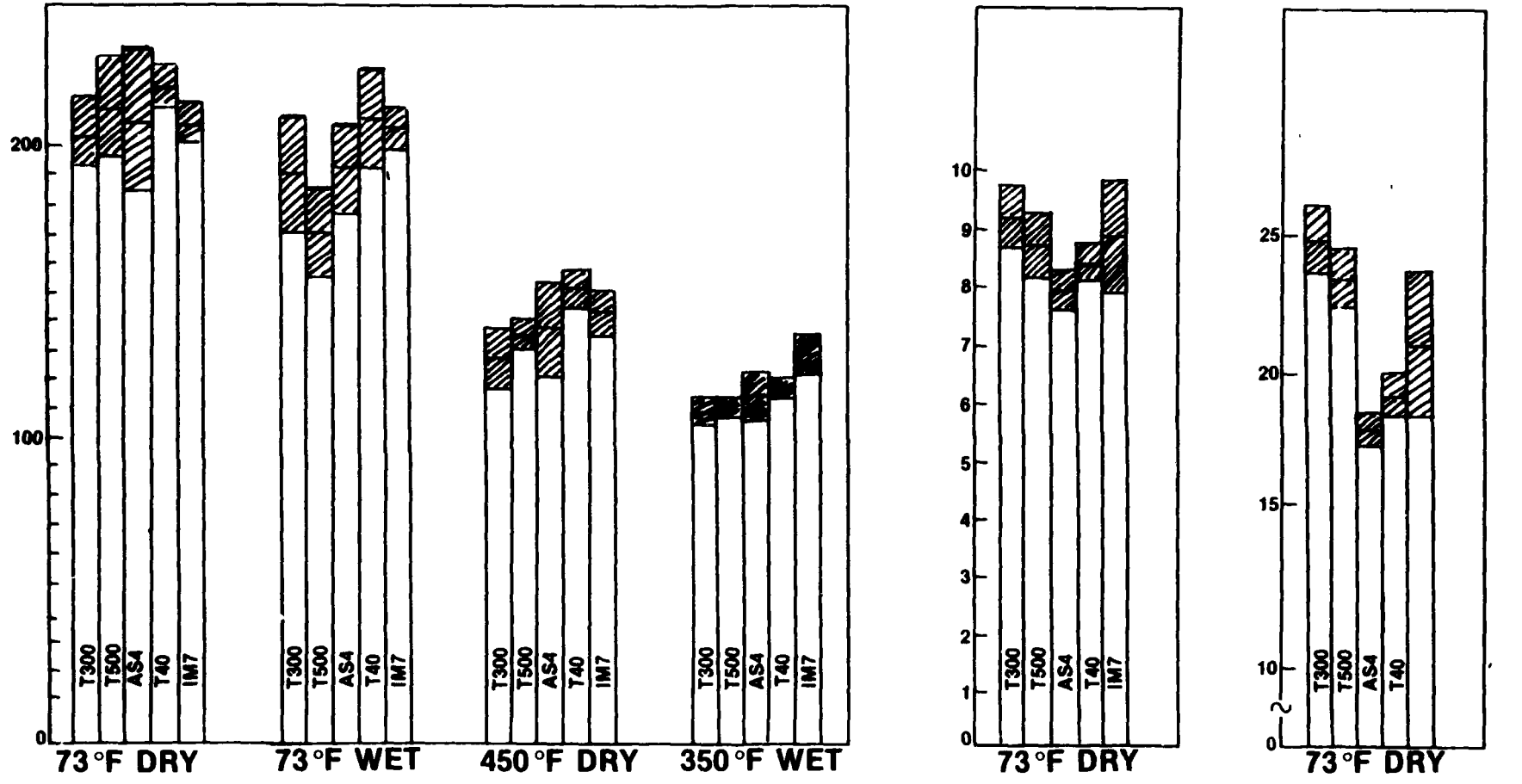


FIGURE 5.2 CATB-44 LAMINATE PROPERTIES VS. FIBER TYPE

best resistance to delamination with strengths of 25 and 24 ksi, respectively. AS-4/CATB-44 at 18 ksi was the lowest. The large scatter for IM7/CATB-44 may be the result of a lack of clear definition of crack initiation in this material. Complete data are shown in Table 5.6 and Figure 5.2.

0° Unidirectional Compression Strength

0° compression strength measurements were made on eight ply, tabbed specimens following the Boeing BMS-8-212E specification. The untabbed test region was 0.188 inches in length. Tests were conducted at 73 and 450°F on dry specimens and at 73 and 350°F on specimens exposed for 2 weeks in water at 160°F. Hot/wet testing was initiated after a temperature equilibration period of two minutes. Five replicate tests were performed on each laminate at each condition. Complete results are shown in Table 5.6 and Figure 5.2.

A slight overall strength advantage is seen with the higher fiber modulus materials, T40/CATB-44 and IM7/CATB-44. No obvious trend in data is seen to indicate a performance difference due to fiber sizing or shape contributions. Due to the significantly higher modulus of both T40 and IM7 fiber, the slight strength advantage shown by their CATB laminates does not translate into an increased strain capability for these materials.

Fractography

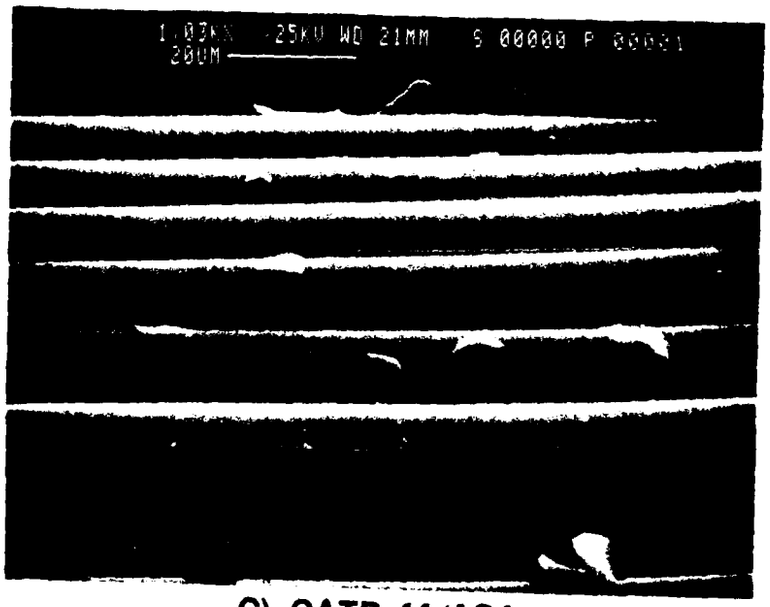
Photomicrographs of selected compression interlaminar shear failure surfaces were obtained by SEM. These photomicrographs are shown in Figures 5.3A through 5.3E.

A mixed mode fracture surface was seen for the T300/CATB-44 and T500/CATB-44 specimens: the crack passed partially through the resin and partially along the interface. The AS-4/CATB-44 failure mode was primarily interfacial. In laminates containing

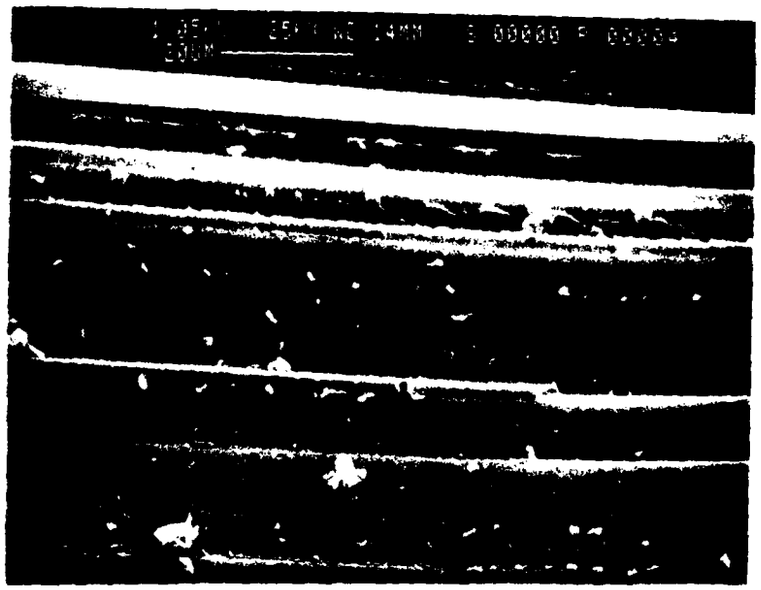
A) CATB 44/T300

B) CATB 44/T500

Figure 5.3
Polished Cross-Sections: CATB 44 Laminates



C) CATB 44/AS4



D) CATB 44/IM7

Figure 5.3
CILS Fracture Surface: CATB 44 Laminates (CONTINUES)

E) CATB 44/T40

Figure 5.3
CILS Fracture Surface: CATB 44 Laminates (CONCLUDED)

higher modulus fibers, T40/CATB-44 and IM7/CATB-44, features intermediate between the AS-4 and the T300/T500 laminates were seen. These observations coincide to a large degree with the matrix/interface dominated properties measured in this study.

5.2.5 Summary of Results

High quality composite laminates with resin contents of 33±2% were fabricated from CATB-44 matrix resin and five commercial carbon fibers. These laminates were evaluated for their matrix/interface dominated mechanical properties and in-plane response to hot and hot/wet conditions. Laminates fabricated from CATB-44 and Amoco T300 and T500 fiber exhibited improved toughness over AS-4/CATB-44 as measured by edge delamination testing and improved fiber/matrix adhesion as measured by shear testing. The higher modulus fiber laminates, made from T40 and IM7, were intermediate in these properties. Fractography also indicated superior fiber/matrix adhesion in T300 and T500 laminates.

In-plane unidirectional compression strength measurements indicated a slight advantage to the use of higher modulus fibers. However, because of their high modulus, their higher strength does not translate into higher strain capability and so the apparent advantages of T40 and IM7 may not hold.

5.2.6 Recommendation of Fiber for Scale-up

The CATB-44/fiber combination with the lowest overall property ranking was CATB-44/AS-4. Therefore, the use of AS-4 fiber was not recommended.

The redirection of work in this program was mainly predicated on improving the resin/interface dominated properties of CATB-44 laminates in order to increase toughness and to allow a higher postcure temperature to enhance elevated temperataure performance. The fiber/resin combinations that best achieved these goals were

CATB-44/T300 and CATB-44/T500. However, since in-plane properties would also affect the overall utility of a prepreg, high modulus fiber was also of interest.

Based on these results, and with the approval of the Project Scientist, Amoco's T300 and Hercules' IM7 were chosen for prepreg scale-up.

5.3 PREPREG PRODUCTION

Two thirty-pound lots of prepreg were produced at Cyanamid's Saugus, CA production facility. The resin was CATB-44 and Amoco's T300 and Hercules' IM7 fibers were used to produce the two lots. Five pounds of each prepreg were returned to Cyanamid's Stamford, CT laboratory and evaluated for quality. Once approved, the prepreg was shipped to five airframe manufacturers specified by AFWAL and to AFWAL.

5.3.1 Quality Assurance

Prior to releasing the prepregs for shipment, a small laminate was produced from each prepreg and shear and dynamic mechanical tests were conducted on each to assure prepreg quality. The laminates were 6" x 6" by 20 plies, unidirectional. They were laid up, bagged, cured and postcured following the procedures established for CATB-44. The postcure temperature was 250°C.

The test results are presented in Table 5.7. The laminate glass transition data indicated full and proper cure was achieved. The short beam shear data confirmed the integrity of the CATB-44 laminates.

5.3.2 Recipients

The following airframe manufacturers received four pounds each of T300/CATB-44 and IM7/CATB-44 prepreg:

TABLE 5.7

CATB-44 TASK IV PREPREG LAMINATE QUALITY SCREEN

Property	Method	Test Condition	Units	Value CATB-44/T300 Lot 1211	CATB-44/IM7 Lot 1210
Tg by DMA					
TAN DELTA	ASTM	Dry	°F	583	601
Modulus Intersect	D4056	90° Direction		502	484
5% Modulus Offset				478	482
Short Beam Shear Strength	ASTM D2344	73°F, Dry	ksi	17.4 ± 0.2	16.6 ± 0.2

± Values are 90% C.L. Layup = $(0)_{20}$

1. Ms. Gail Dolan
   McDonnell Aircraft Co.
   357/32/3/345
   P.O. Box 516
   St. Louis, MO 63166
   (314)233-1848

2. Ms. Mary E. Harb
   McDonnell Douglas Astronautics Co. - St. Louis Div.
   Mail Stop E467/101/MEZ/E51
   P.O. Box 516
   St. Louis, MO 63166
   (314)234-1218

3. Mr. John Wannamaker
   Lockheed California Co.
   Bldg. 369/B6
   P.O. Box 551
   Burbank, CA 91520
   (818)955-7908

4. Mr. Jack Reynolds
   General Dynamics, Ft. Worth Div.
   Mail Zone 5860
   P.O. Box 748
   Fort Worth, TX 76101
   (817)777-3521

5. Ms. Ann Beck
   Northrop Aircraft Div.
   One Northrop Ave.
   Dept. 3874, Zone 62
   Hawthorne, CA 90250-3277
   (213)332-4963

Five pounds of each prepreg were sent to AFWAL:

Dr. Charles Lee
AFWAL/MLBC
Wright Patterson Air Force Base
Ohio 45433
(513)255-9075

Quality control data were included on each roll of prepreg including: resin content, flow, gel time and volatile content.

5.4 FILM INTERLEAFED LAMINATES

A systems engineering approach to toughening composite materials through incorporation of thin, discrete, high strain film interleafs has been investigated by Cyanamid [79]. The investigations results in improvements on the work of others. Reductions in impact damage and delamination failure had been found when adhesive layers were placed between the plies of a composite. Cyanamid's improvements included reducing the thickness of the film interleaf to 0.0005-0.0010 inches, resulting in a composite with desirable resin content, and developing film interleafs with the ability to perform under severe conditions of heat, moisture and solvent exposure.

The effect of incorporating interleafs in the CATB-44 laminates was investigated. The edge delamination resistance of composites prepared from CATB-44 matrix resin on Amoco T300 fiber and CATB-44 on Hercules IM7 fiber was measured. These evaluations indicated the potential for toughness enhancement of CATB-44 laminates by this approach.

Materials

The two prepreg materials chosen for this evaluation were:

1.	Matrix:	CATB-44
	Fiber:	Amoco T300, UC309
	Resin Content:	34±2% by weight
	Fiber Areal Weight:	145±2 gm/m^2
2.	Matrix:	CATB-44
	Fiber:	Hercules IM7 "G"
	Resin Content:	34±2% by weight
	Fiber Areal Weight:	145±2 gm/m^2

The interleaf film chosen for this evaluation was a proprietary thermoplastic with a thickness of 0.0005 inches.

Specimen Preparation

Two edge delamination (ED) laminates were prepared from each prepreg material: a control, uninterleafed panel and an interleafed panel. The laminate stacking sequence was $(+30,-30_2,+30,90_2)_s$. The panels were 12 inches square. The interleafed panels had film at each ply interface.

The laminates were bagged and cured using the previously described procedures. The test laminates were postcured unrestrained in a circulating air oven for 4 hours at 250°C.

Five test coupons, 1-1/2 inches in width by 10 inches in length were prepared from each panel. The specimen edges were finished smooth by wet polishing with 600 grit emery paper. The coupons were then dried for 48 hours at 71°C to ensure their dry state.

The specimen edges were painted with white ink to assist in crack detection. They were tested on an MTS Model 810 Servo-Hydraulic test machine equipped with hydraulic wedge-action grips. The speed of test was 0.05 inches per minute. Failure was detected visually and confirmed by a change in the slope of the load-deformation curve. The force at crack initiation was measured.

Test Results and Discussion

The results of these evaluations are presented in Table 5.8. Earlier results on CATB-44 on Hercules AS-4 fiber, determined in Task III are included for comparison. The laminates for this interleaf study were postcured at 250°C; the laminates in Task III were postcured at 230°C. The higher postcure temperature would be expected to cause a higher laminate Tg. This means that it would have higher residual stresses which would cause a lower edge delamination stress (EDS).

A comparison of EDS between the uninterleafed controls showed T300/CATB-44 to be 24% more delamination resistant than IM7/CATB-44. This result was expected because previous data showed that T300 fiber had better adhesion to CATB-44 than did IM7.

Interleafing marginally improved the EDS of both composite constructions. The increase in EDS with interleafing was 10% for T300/CATB-44 and 8% for IM7/CATB-44. The failure modes of all four systems were the common intraply, stepped, longitudinal delaminations typically observed in this test with no interleaf debonding observed. Previous work [80] showed that this degree of improvement in edge delamination resistance can be associated with significant improvements in composite impact performance.

Thus, this evaluation identified a film interleaf that was compatible with CATB-44 and provided improved composite performance.

TABLE 5.8

EDGE DELAMINATION TEST RESULTS - CATB-44 COMPOSITE INTERLEAFING STUDY

Material Identification	Edge Delamination Stress at First Crack, (ksi) Control	Film "E" Interleaf
CATB-44/AS-4*, Lot 847	21.8 $\pm$ 0.5	--
CATB-44/T300, Lot 1211	22.3 $\pm$ 0.5	24.4 $\pm$ 0.5
CATB-44/IM7, Lot 1210	18.0 $\pm$ 0.8	19.4 $\pm$ 0.6

Lay-up = $(+30, -30_2, +30, 90_2)_s$

*Data from Task III -- Postcured at 230°C

6.0 CONCLUSIONS

1. Acetylene terminated resins are well known for their excellent high temperature properties especially under hot/wet conditions. However, their brittleness has restricted their use. Through formulation, it was possible to obtain a more favorable balance between composite properties at elevated temperatures and resistance to delamination.

2. The formulated resin that was scaled-up to prepreg during this program, designated CATB-44, had good high temperature properties: 0° flexural strength at 230°C (450°F) of 676 KPa (98 ksi) after wet conditioning, it did not embrittle after 200 hr. at 204°C (400°F), and had excellent thermal spike resistance. These properties were superior to the properties of CYCOM 3100 (BMI) and CYCOM 985 (epoxy).

3. AS-4/CATB-44 also had a delamination resistance falling midway between the BMI and epoxy matrix composites.

4. By altering the fiber, significant improvements were found in edge delamination strength. Laminates containing Amoco's T300 and T500 had a stress at first crack 35% higher than those containing Hercules' AS-4 fiber. Among the intermediate modulus fibers, IM7 was slightly better than T40.

5. The AT resins were successfully interleafed with a thermoplastic interleaf and some improvements in Mode I dominated, edge delamination strength were noted. Even greater improvements would be expected if impact damage and/or compression strength after impact were assessed. A minimal detrimental effect on structural properties such as compression strength would be expected.

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APPENDIX A - NEAT RESIN TEST METHODS

OUT-TIME

All AT resin formulations were mixed at 120-150°C for 2-5 minutes and then allowed to stand at 24°C (75°F) for out-time measurements. Samples were periodically checked for tack and the resin system was considered to have advanced if it lost tack, and did not flow on warming.

APPEARANCE AFTER AGING

From each preliminary screening formulation, one cured coupon was aged at 350°F for two weeks followed by 30 h at 450°F and then tested at room temperature under flexure. After the test, the broken coupon was visually examined for discoloration, cracking or voids.

RHEOLOGICAL PROFILES

The standard operating procedure for measuring the rheological profiles of resin used a Rheometrics Mechanical Spectrometer with the following conditions:

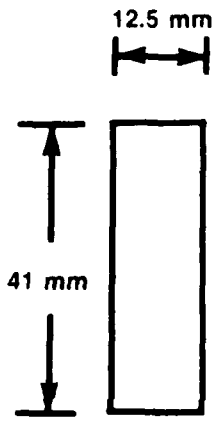
Gap Size:	1 mm
Parallel Plate Diameter:	50 mm
Frequency:	1 Hz
Strain:	30%
Heating Rate:	2°C/min
Starting Temperature:	70°C
Recorded Temperature:	Over Temperature Range
Plotted Output:	Log (Viscosity*) vs. Temperature
Printed Output:	G', G", Viscosity*, Torque, Time, Temperature

Cure profiles were run until a well defined minimum in the viscosity curve was established.

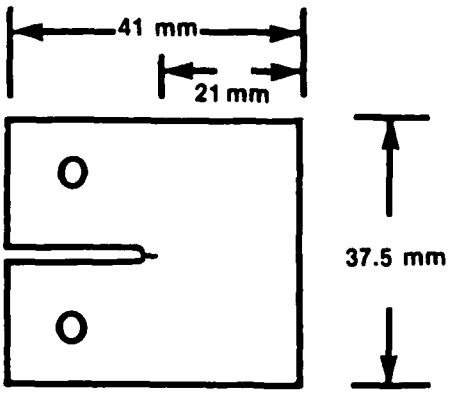
DYNAMIC MECHANICAL ANALYSIS (DMA)

The dynamic mechanical profiles of resins were obtained using DuPont's Model 982 Dynamic Mechanical Analyzer. An ASTM procedure for dynamic mechanical analysis is given in ASTM D4065. A bar of the neat resin (12.5 mm x 37 mm x 1.6 mm) was held by two arms, and one arm was driven at a constant amplitude. The specimen is shown in Figure A-1. The frequency of vibration of the system was monitored as was the power required to maintain that amplitude (i.e., the damping). Frequency was related to the sample's modulus and damping was related to mechanical loss in the sample. Dynamic mechanical profiles were obtained by heating the sample in nitrogen from a low temperature (usually either -100°C or 23°C) to a high temperature (above the glass transition temperature) at a rate of 5°C/min. The modulus and tan delta (loss parameter) were then plotted as a function of temperature. The glass transition temperature, Tg, was defined as the temperature at which tan delta reached a maximum. Other characteristic temperatures measured from the modulus curve were the modulus intercept and the 5% offset as shown in Figure A-2. These latter two values were considered to be more significant for determining upper use temperature as defined by composite mechanical performance.

A specimen can be analyzed either dry or after wet conditioning. Wet conditioning of specimens is done by immersing the specimen in distilled water at 71°C (160°F) for two weeks. The DMA profiles of the resins are primarily used to determine Tg and the modulus profile. However, they can also be used to study such things as phase separation, or the effect of additives.



FLEXURE,
DMA



COMPACT TENSION
FRACTURE TOUGHNESS

(Specimen Thickness: 6 mm)

RESIN SCREEN TEST SPECIMENS
FIGURE A1

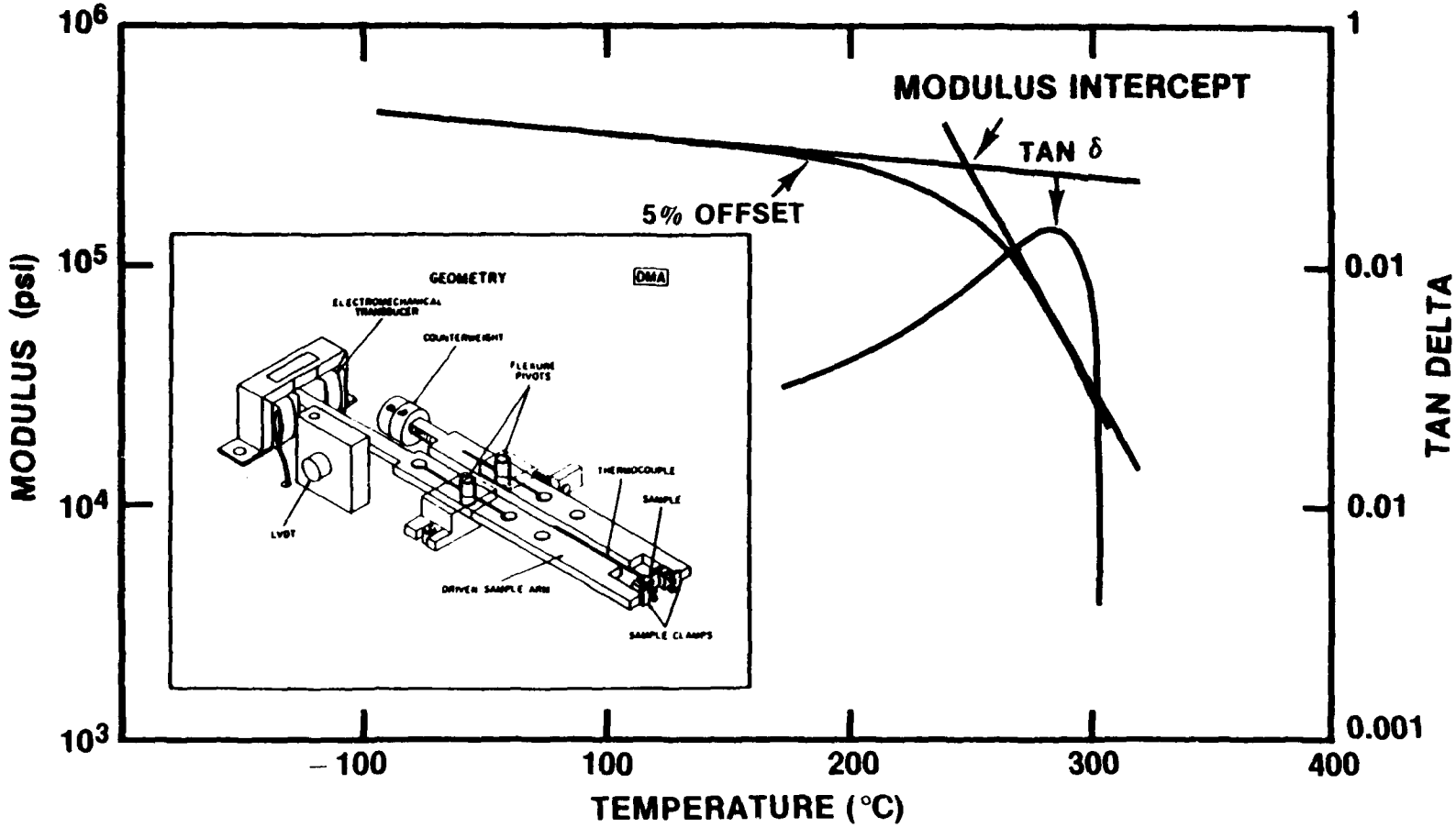


FIGURE A2 **DYNAMIC MECHANICAL ANALYSIS**

FLEXURE

The flexural test was used to provide data on the stress-strain behavior of the resin. Basic properties obtained are modulus, offset yield stress, and strain, yield stress and strain, failure strength and failure strain, and area under the stress strain curve (or work to break). The specimens are 12.5 mm x 37 mm x 1.6 mm and are simple to machine (being rectangular). Six specimens are used in each test. The strain rate used is 10%/min. The test procedures and equations for the calculation of properties are given in ASTM D790. The data from each of the six individual flexural bars is checked for outliers, averaged, and the 95% confidence calculated.

Testing of water conditioned specimens is carried out in an immersion tank, reducing the water loss during testing. The same tank is used for higher temperature tests with an oil bath. For the highest temperature testing an oven is used to maintain temperature. Normally a two minute soak in the water or oil bath is used to equilibrate the sample to temperature.

Several flexural stress-strain properties correlate to important composite properties. Resin modulus has been found to correlate to composite compression strength. For single phase systems, the resin's strain-to-failure is related to the compression strength after impact of its composites.

FRACTURE TOUGHNESS SPECIMEN

The compact tensile specimen was used to measure the plane-strain fracture toughness, K_{IC}, of a neat resin. The specimen geometry and size as well as the test procedure is described in ASTM E399. The specimen, shown in Figure A-1, is 1.6 mm x 41 mm x 38 mm. A notch is cut using a diamond cutting wheel, and is extended using a jeweler's saw. The final notch tip is introduced by wedging a razor blade into the jeweler's saw cut and "popping

in" a crack. This gives a crack tip whose radius is characteristic of the material. The length of the crack is measured after the sample has been broken.

The plane strain fracture toughness, K_{IC}, is an indication of the energy required to cause a pre-existing crack to grow. This relates to the growth of interlaminar cracks in composites and is useful in evaluating resins that have two phase structure.

WATER ABSORPTION

The weight percent of water absorbed is measured on all resins after exposure to the conditioning environment, which consists of immersion in distilled water at 71°C (160°F) for 2 weeks. The procedure is as follows. Generally, six flexural test bars and 2 DMA bars are placed in water. To determine water pick-up, the DMA bars are cleaned with distilled water, dried, and weighed together on an analytical balance to the nearest 0.1 mg. They are then placed in water, with the flex bars, for exposure. After exposure the DMA bars are removed and patted dry using a lint free tissue and weighed again. The weight percent of water absorbed is the weight change divided by the original weight times one hundred.

APPENDIX B - PREPREG AND LAMINATE CHARACTERIZATION TEST METHODS

PREPREG CHARACTERIZATION METHODS

RESIN CONTENT/FIBER AREAL WEIGHT

Resin content and carbon fiber areal weight are determined from (3) 3x12 inch samples of prepreg. After weighing the squares, the resin matrix is dissolved in methylene chloride. The washing process involves washing the samples in 5 separate baths of methylene chloride for 5 min. each for a total of 25 minutes. After the fibers are clean, they are air dried in an air circulating oven for 20 min. at 300±25°F. The samples are then allowed to cool to room temperature in a desiccator before weighing. The samples are then reweighed and calculations are performed to determine resin content and fiber areal weight.

VOLATILE CONTENT

Volatile content is determined by hanging a preweighed piece of prepreg (4x4 inch) in an air circulating oven at 300±25°F for 15 minutes. The prepreg is covered at the point of attachment by a small piece of Armalon to prevent damage to the specimen. After the drying period the prepreg is allowed to cool to room temperature in a desiccator before the sample is weighed again. The sample is then weighed and volatile content calculations are derived from these values. Three specimens are measured.

RESIN FLOW

Four pieces of prepreg, each 4x4 inches are used to determine flow. The pieces are stacked in a 0, 90, 0, 90 configuration and the sample is weighed. The flow specimen is constructed in the following manner: 2 plies 7781 glass fabric, 1 ply TX 1040, stacked prepreg sample, 1 ply TX 1040, 2 plies 7781 glass fabric. The entire layup is then placed in a press at 350±5°F and 100±5

psi for 5 min. plus the resin gel time. After the sample has been removed, it is allowed to cool to room temperature between two metal plates. The flash is removed, the sample reweighed and flow (the percent weight lost) is calculated.

GEL TIME

A Fisher-Johns melting point apparatus is set at 350±5°F and a 0.25 x 0.25 inch sample of prepreg sandwiched between two glass covers is placed on the heating platform. The gel point is reached when no resin movement is observed through the cover glass when moderate pressure is applied to the sample.

TACK

Two three-inch by three-inch squares of prepreg are cut. They are pressed together with a force of 10 pounds for 10 seconds. The pieces should adhere to each other. If the pieces do not, press them together with a force of 50 pounds for 10 seconds. Report the force at which the pieces adhere, or report no adherence at 50 pounds. Test at 73±5°F.

OUT- TIME

Out-time at 23°C/50% RH is determined by measuring the time over which the prepreg still passes the tack test. Out time tests are conducted at 7, 14, 21 and 28 day intervals.

LAMINATE CHARACTERIZATION METHODS

0° FLEXURAL STRENGTH AND MODULUS

The flexural test described in ASTM D790-81, Method II [76], has been widely used as a screening test for composite performance.

The laminate stacking sequence for the 0° flexure tests was $(0)_{16}$. The specimen was 5 by 0.5 inches. The test span is 40 times the specimen thickness and 4-point loading is applied following ASTM D790-81, Method II, as shown in Figure B-1. Midspan deflection is monitored by an LVDT transducer. Strength, strain, and modulus are calculated using the equations found in ASTM D790-81, Method II.

FOUR-POINT INTERLAMINAR SHEAR TEST

Interlaminar shear strength is determined using the 4-point loading method developed by C.E. Browning, et al., and described in ASTM STP 797 [77]. This method retains the attractive features of the standard ASTM D2344 [73] Short Beam Shear test while consistently producing an interlaminar shear failure mode.

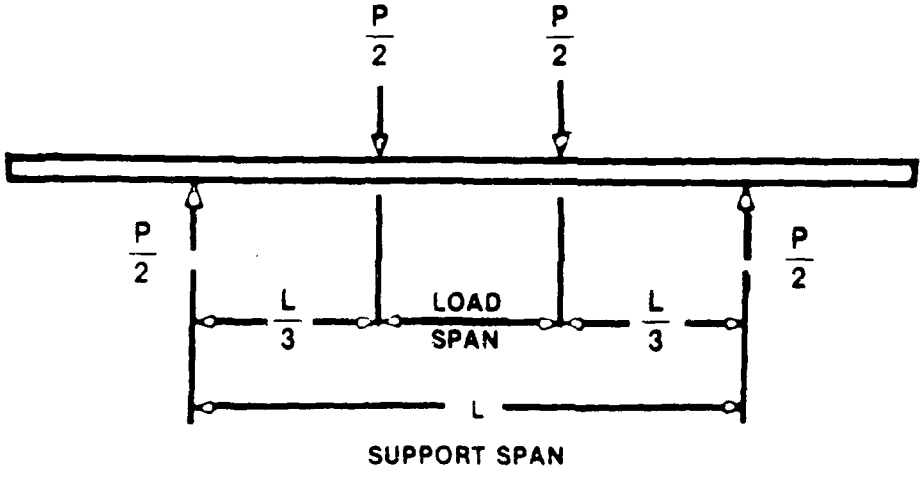
The test specimens have a laminate stacking sequence of $(0)_{16}$, a length of 3 in. and a width of 0.5 in., as shown in Figure B-2. The test span is 16 times the specimen thickness, and the load is applied at the quarter points of the test span.

90° FLEXURAL STRENGTH AND MODULUS

The laminate stacking sequence for the 90° flexure test is $(90)_{16}$. The specimen width is 1.0 in., and the length is 4 in. The test span is 40 times the specimen thickness, and 4-point loading is applied following ASTM D790-81, Method II, as shown in Figure B-1. Midspan strain is monitored by a strain gage interfaced to an Instron X-Y recorder. Calculations of strength, strain, and modulus are made using the equations in ASTM D790, Method II.

MODE I STRAIN ENERGY RELEASE RATE TESTS

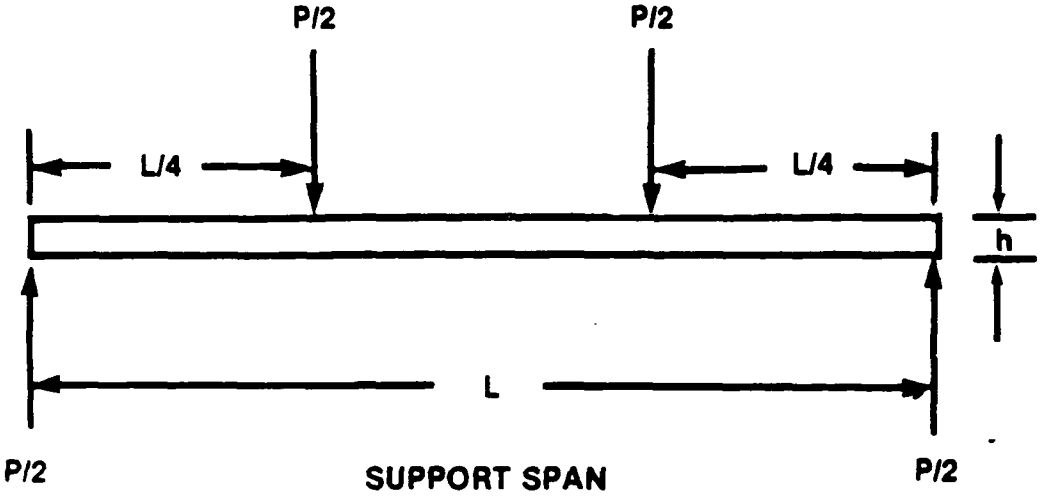
Hinged double cantilever beam specimens (Figure B-3) are used to determine G_{IC} experimentally. The specimen used in this



1) LAMINATE STACKING SEQUENCE: $(0°)_{16}$
   SPECIMEN WIDTH: .5"
   SUPPORT SPAN: 40 TIMES SPECIMEN THICKNESS

2) LAMINATE STACKING SEQUENCE: $(90°)_{16}$
   SPECIMEN WIDTH: 1.0"
   SUPPORT SPAN: 32 TIMES SPECIMEN THICKNESS

FIGURE B-1
FLEXURAL TEST SPECIMENS-ASTM D790 METHOD II



LAMINATE STACKING SEQUENCE: $(0°)_{16}$
SPECIMEN WIDTH: .5"
SUPPORT SPAN: 16 TIMES SPECIMEN THICKNESS

FIGURE B-2
INTERLAMINAR (FOUR POINT) SHEAR TEST SPECIMEN

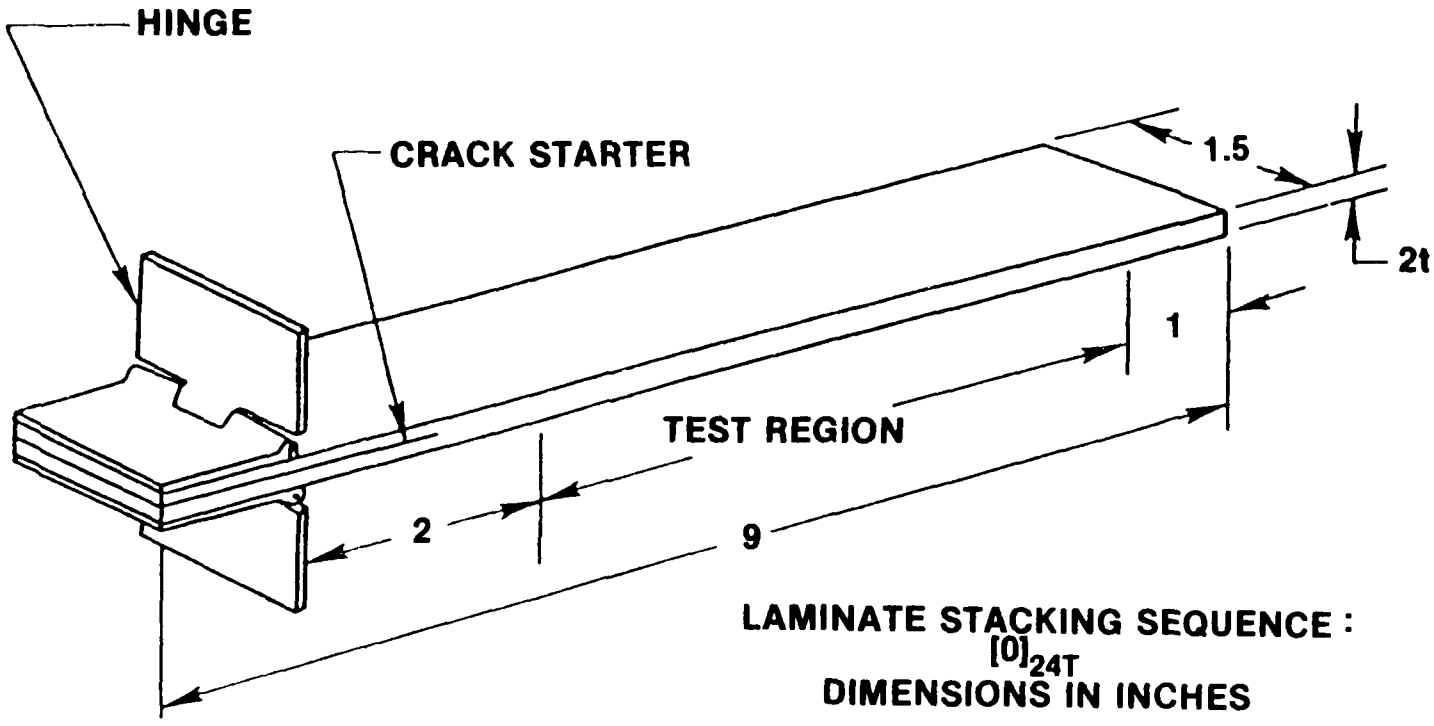


FIGURE B-3
MODE I DOUBLE CANTILEVER BEAM SPECIMEN

program is 1.5 in. wide by 9.0 in. long, and 24 plies thick. A 1 mil thick crack starter is placed between the two center layers of the laminate. Hinged tabs attached to the specimen are used to mount the specimen in the test machine. This ensures that no bending moments are applied to the specimen surface and eliminates Mode II load components.

The test is run in displacement control and the load-deflection curve is recorded. The test procedure and the energy area integration method of computing G_{IC} outlined in NASA 1092 [78] was used in the calculations.

EDGE DELAMINATION TESTS

This test uses laminates and test procedures which are currently being used by the Air Force Materials Laboratory. Specimens used in this program, shown in Figure B-4, are 1-1/2 in. wide by 10 in. long and 12-plies thick. The untabbed laminates have a $[+30/-30_2/+30/90_2]_s$ stacking sequence. Specimens are loaded in axial tension on a Model 1125 Instron Universal Test Machine at a crosshead displacement rate of 0.05 in./min. An extensometer with a 1.0 in. gage length is used to measure nominal strain. In addition, the usual delamination and failure stresses are measured.

The test procedure employed in these tests is straightforward. The load cell and extensometer output are recorded on an x-y plotter as the specimen is loaded. Loading continues until visible detection of edge delamination and the corresponding abrupt deviation in the load-strain plot occurs. The strain and load at the onset of delamination (E_c) are recorded, and the stress is calculated by normalizing the load by the cross-sectional area.

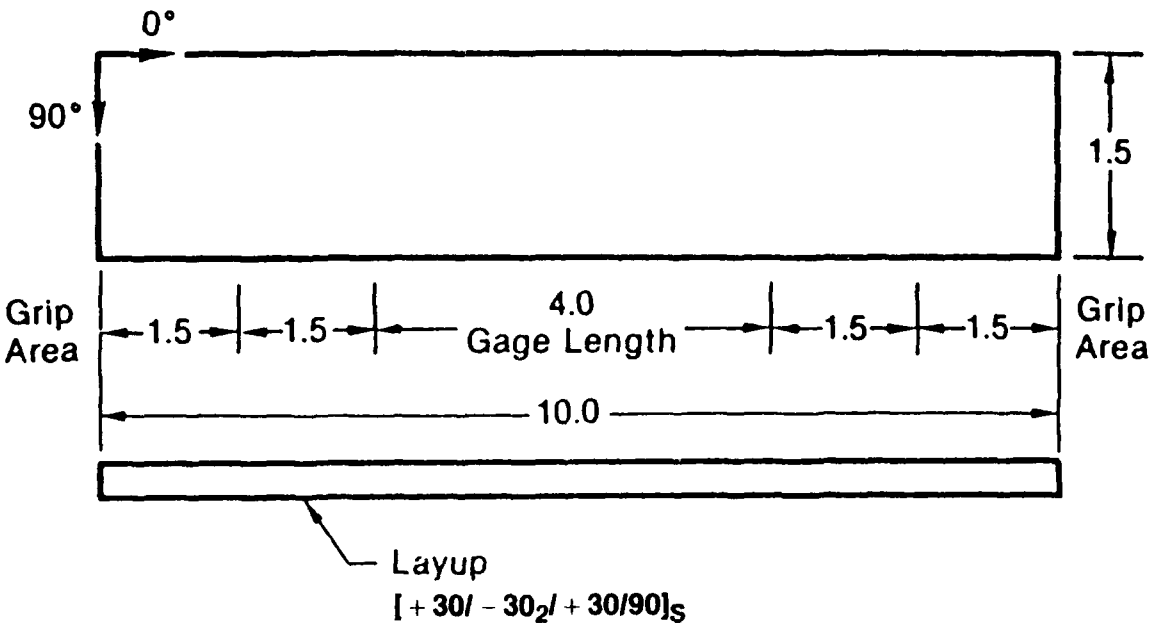


FIGURE B-4
EDGE DELAMINATION SPECIMEN

IN-PLANE SHEAR PROPERTIES

Laminate in-plane shear properties are determined following the procedures set forth in ASTM D3518 [73]. The method is based on the uniaxial tensile stress-strain response of a $\pm 45^\circ$ laminate which is symmetrically laminated about the midplane. Through the use of relations derived from laminated plate theory, shear stress-strain curves are obtained from a uniaxial tension test of a $\pm 45^\circ$ laminate using stress; longitudinal and transverse strain outputs.

The test specimens of ASTM D3039, referenced in ASTM D3518, are used. The specimen has a stacking sequence of $(\pm 45_2)_s$. The specimen is 225 mm long and 25 mm wide. Tapered tabs are applied leaving a test length of 150 mm. Specimen geometry is shown in Figure B-5. Longitudinal and transverse strains are measured by a DSST GP biaxial extensometer, 25 mm gage length, with elevated temperature capability.

THERMAL AGING TESTS

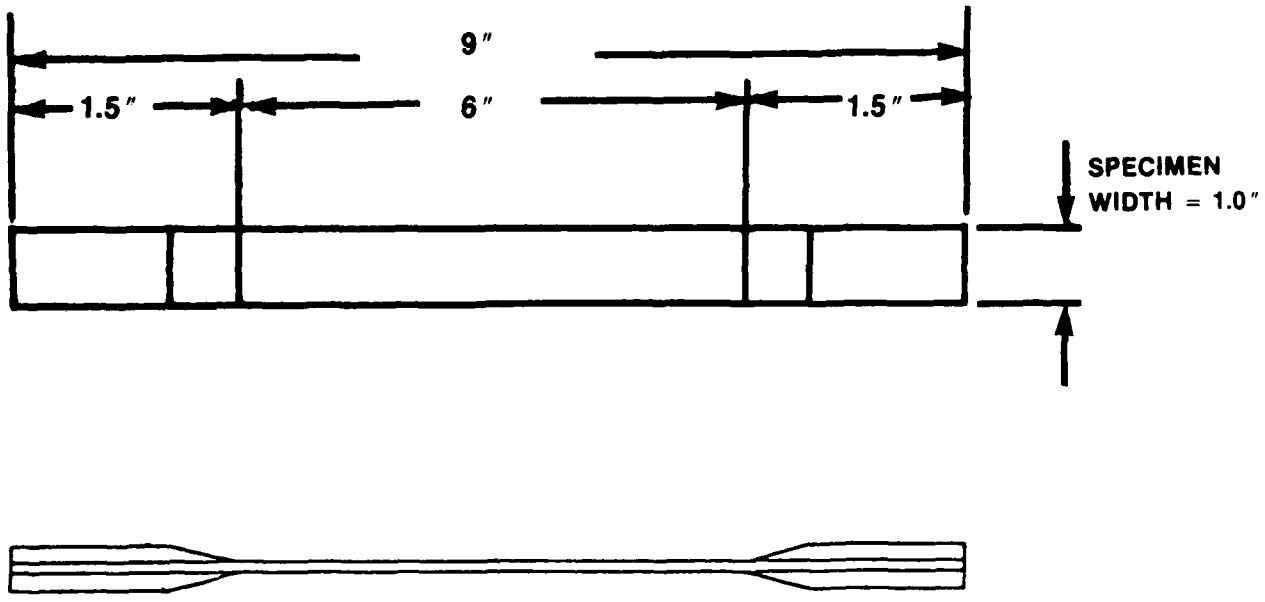
Four one-inch by two inch specimens $(0/\pm 45/0)_s$ are subjected to thermal aging, two specimens each at the following conditions:

Condition I

- Expose for 25 hours at 350°F, then
- Expose for 264 hours at 275°F

Condition II

- Expose for 25 hours at 450°F, then
- Expose for 264 hours at 275°F



LAMINATE STACKING SEQUENCE: $(\pm 45_2)_s$
TAB THICKNESS: 1.5 TIMES SPECIMEN THICKNESS

FIGURE B-5
IN-PLANE SHEAR TEST SPECIMEN-ASTM D3518

Following these exposures, the specimen edges are polished and inspected for microcracking using 250x photomicrographs.

THERMAL SPIKE TEST

Three one-inch by two-inch specimens, $(0/\pm 45/0)_s$, are exposed to 71°C, 75% RH for 56 days. Two of these specimens are immersed in 177°C silicone oil for 1 minute every 3.5 days from the start of exposure and returned to 71°C, 75% RH for a total of 10 cycles. The third specimen is a control, and is not thermally spiked. Moisture gain readings are taken on all three specimens prior to each thermal spike and the end of 56 days. Total moisture gain over the course of the test is measured, and comparisons of gain between the control and thermally spiked specimens are made.

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